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ELEMENTARY TREATISE  
ON  
NATURAL PHILOSOPHY.





ELEMENTARY TREATISE  
ON  
NATURAL PHILOSOPHY

BASED ON THE TRAÎTÉ DE PHYSIQUE OF

A. PRIVAT DESCHANEL

FORMERLY PROFESSOR OF PHYSICS IN THE LYCÉE LOUIS-LE-GRAND,  
INSPECTOR OF THE ACADEMY OF PARIS.

BY

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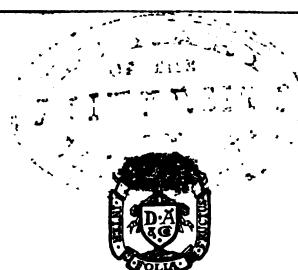
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PART II.

HEAT.

*THIRTEENTH EDITION.*

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NEW YORK:  
D. APPLETON AND COMPANY,  
1898.

P.12.  
1876  
V.1.

*Authorised Edition.*

78062

## PREFACE TO THE THIRTEENTH EDITION OF PART II.

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This edition contains a new chapter on Thermodynamics, in which free use is made of the methods of the Differential Calculus. Entropy is explained, and several examples are given of the deduction of physical relations by changing the order of differentiation.

Among the additions in other parts of the book are:—

Bunsen's calorimeter figured and described;

Dewar's experiments on liquid oxygen;

Rowland's determination of the mechanical equivalent of heat, and of the specific heat of water at various temperatures, the minimum specific heat being attained at about 30° C.;

Thomson and Joule's experiments on forcing gases through a cotton wool plug, to determine the difference between the cooling effect of expansion and the work done in the expansion;

Van der Waals' theory with respect to the departure of gases from Boyle's law.

To prevent the book from becoming too large, the account of Melloni's experiments is curtailed; and a number of details respecting steam-engines are omitted.

The pages and sections of Part II. are now numbered from 1 onwards, instead of making the numbers consecutive to those in Part I.

BELFAST, January, 1894.



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**UNIVERSITY OF CALIFORNIA**  
**DEPARTMENT OF PHYSICS**

**H E A T.**

**C H A P T E R I.**

**THERMOMETRY.**

**1. Heat—Cold.**—The words *heat* and *cold* express sensations so well known as to need no explanation; but these sensations are modified by subjective causes, and do not furnish an invariable criterion of objective reality. In fact, we may often see one person suffer from heat while another complains of cold. Even for the same person the sensations of heat and cold are comparative. A temperature of 50° Fahr. suddenly occurring amid the heat of summer produces a very decided sensation of cold, whereas the same temperature in winter has exactly the opposite effect. We may mention an old experiment upon this subject, which is at once simple and instructive. If we plunge one hand into water at 32° Fahr., and the other into water at about 100°; and if after having left them some time in this position we immerse them simultaneously in water at 70°, they will experience very different sensations. The hand which was formerly in the cold water now experiences a sensation of heat; that which was in the hot water experiences a sensation of cold, though both are in the same medium. This plainly shows that the sensations of heat and cold are modified by the condition of the observer, and consequently cannot serve as a sure guide in the study of calorific phenomena. Recourse must therefore be had to some more constant standard of reference, and such a standard is furnished by the thermometer.

**2. Temperature.**—If several bodies heated to different degrees are placed in presence of each other, an interchange of heat takes place between them, by which they undergo modifications of opposite kinds; those that are hottest grow cooler, and those that are coldest grow warmer; and after a longer or shorter time these inverse phenomena cease to take place, and the bodies come to a state of mutual

equilibrium. They are then said to be at the same *temperature*. If a source of heat is now brought to act upon them, their temperature is said to *rise*; if they are left to themselves in a colder medium, they all grow cold, and their temperature is said to *fall*. *Two bodies are said to have the same temperature if when they are placed in contact no heat passes from the one to the other.* If when two bodies are placed in contact heat passes from one to the other, that which gives heat to the other is said to have the higher temperature. Heat always tends to pass from bodies of higher to those of lower temperature.

**3. Expansion.**—At the same time that bodies undergo these changes in temperature, which may be verified by the different impressions which they make upon our organs, they are subjected to other modifications which admit of direct measurement, and which serve as a means of estimating the changes of temperature themselves. These modifications are of different kinds, and we shall have occasion to speak of them all in the course of this work; but that which is especially used as the basis of thermometric measurement is change of volume. In general, when a body is heated, it increases in volume; and, on the other hand, when it is cooled its volume diminishes. The expansion of bodies under the action of heat may be illustrated by the following experiments.

**1. Solid Bodies.**—We take a ring through which a metal sphere



Fig. 1.—Gravesande's Ring.

just passes. This latter is heated by holding it over a spirit-lamp, and it is found that after this operation it will no longer pass through the ring. Its volume has increased. If it is now cooled by immersion in water, it resumes its former volume, and will again pass

through the ring. If, while the sphere was hot, we had heated the ring to about the same degree, the ball would still have been able to pass, their relative dimensions being unaltered. This little apparatus is called *Gravesande's Ring*.

**2. Liquids.**—A liquid, as water for instance, is introduced into the

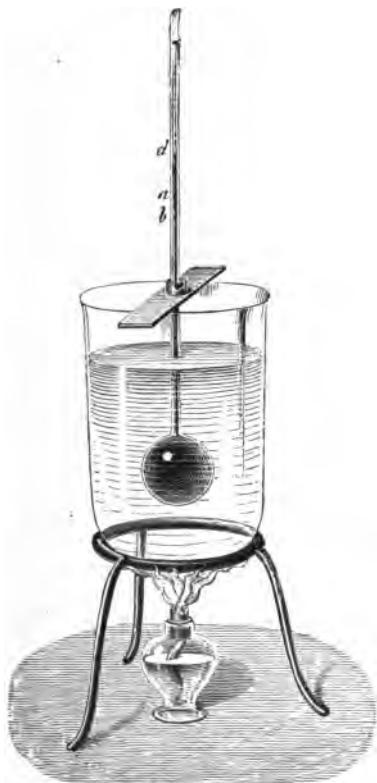


Fig. 2.—Expansion of Liquids.

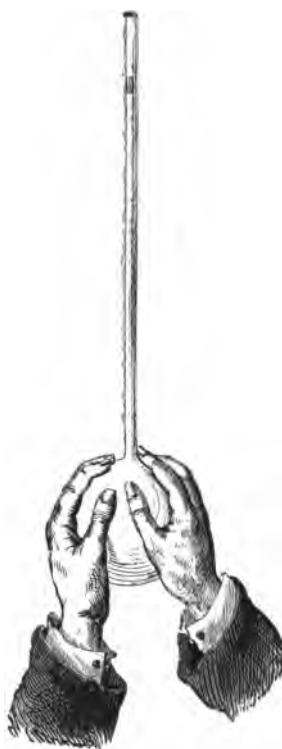


Fig. 3.—Expansion of Gases.

apparatus shown in Fig. 2, so as to fill at once the globe and a portion of the tube as far as *a*. The instrument is then immersed in a vessel containing hot water, and at first the extremity of the liquid column descends for an instant to *b*; but when the experiment has continued for some time, the liquid rises to a point *a'* at a considerable height above. This twofold phenomenon is easily explained. The globe, which receives the first impression of heat, increases in volume before any sensible change can take place in the temperature of the liquid. The liquid consequently is unable to fill the entire

capacity of the globe and tube up to the original mark, and thus the extremity of the liquid column is seen to fall. But the liquid, receiving in its turn the impression of heat, expands also, and as it passes the original mark, we may conclude that it not only expands, but expands more than the vessel which contains it.

3. *Gases.*—The globe in Fig. 3 contains air, which is separated from the external air by a small liquid index. We have only to warm the globe with the hands and the index will be seen to be pushed quickly upwards, thus showing that gases are exceedingly expansible.

4. *General Idea of the Thermometer.*—Since the volume of a body is changed by heat, we may specify its temperature by stating its volume. And the body will not only indicate its own temperature by this means, it will also exhibit the temperature of the bodies

by which it is surrounded, and which are in equilibrium of temperature with it. Any body which gives quantitative indications of temperature may be called a thermometer.

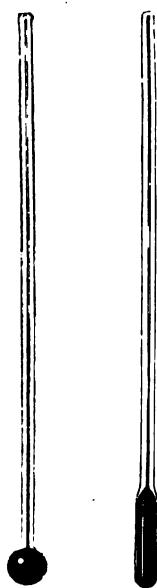


Fig. 4.—Mercurial Thermometers.

scale attached to or engraved on the tube.

6. *Construction of the Mercurial Thermometer.*—The construction of an accurate mercurial thermometer is an operation of great delicacy, and comprises the following processes.

1. *Choice of the Tube.*—The first object is to procure a tube of as uniform bore as possible. In order to test the uniformity of the

bore, a small column of mercury is introduced into the tube, and the length which it occupies in different parts of the tube is measured. If these lengths are not equal, the tube is not of uniform bore. When



Fig. 5.—Introduction of the Mercury.

a thermometer of great precision is required, the tube is *calibrated*; that is, divided into parts of equal volume, by marking upon it the lengths occupied by the column in its different positions.

When a suitable tube has been obtained, a reservoir is either blown

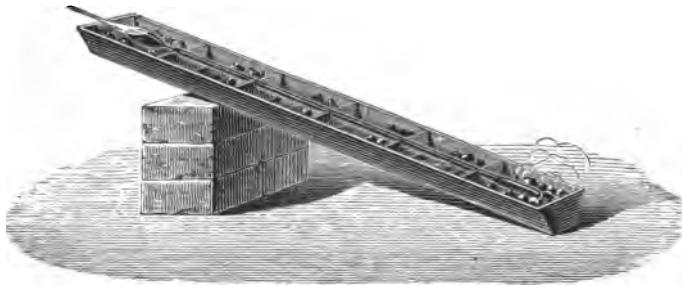


Fig. 6.—Furnace for heating Thermometers.

at one end or attached by melting, the former plan being usually preferable.

**2. Introduction of the Mercury.**—At the upper end of the tube a temporary bulb is blown, and drawn out to a point, at which there is

a small opening. This bulb, and also the permanent bulb, are gently heated, and the point is then immersed in a vessel containing mercury (Fig. 5). The air within the instrument, growing cold, diminishes in expansive force, so that a quantity of mercury is forced into the temporary bulb by the pressure of the atmosphere. The instrument is then set upright, and by alternate heating and cooling of the permanent bulb, a large portion of the mercury is caused to descend into it from the bulb at the top. The instrument is then laid in a sloping position on a special furnace (Fig. 6) till the mercury boils. The vapour of the boiling mercury drives out the air, and when the mercury cools it forms a continuous column, filling the permanent bulb and tube. If any bubbles of air are seen, the operation of boiling and cooling is repeated until they are expelled.

*3. Determination of the Fixed Points.*—The instrument, under these conditions, and with any scale of equal parts marked on the tube, would of course indicate variations of temperature, but these indications would be arbitrary, and two thermometers so constructed would in general give different indications.

In order to insure that the indications of different thermometers

may be identical, it has been agreed to adopt two standard temperatures, which can easily be reproduced and maintained for a considerable time, and to denote them by fixed numbers. These two temperatures are the freezing-point and boiling-point of water; or to speak more strictly, the temperature of melting ice, and the temperature of the steam given off by water boiling under average atmospheric pressure. It has been observed that if the thermometer be surrounded with melting ice (or melting snow), the mercury, under whatever circumstances the ex-

periment is performed, invariably stops at the same point, and remains stationary there as long as the melting continues. This then is a fixed temperature. On the Centigrade scale it is called zero, on Fahrenheit's scale 32°.

In order to mark this point on a thermometer, it is surrounded by melting ice, which is contained in a perforated vessel, so as to allow

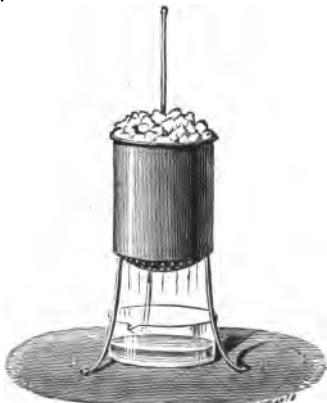


Fig. 7.—Determination of Freezing-point.

the water produced by melting to escape. When the level of the mercury ceases to vary, a mark is made on the tube with a fine diamond at the extremity of the mercurial column. This is frequently called for brevity the *freezing-point*.

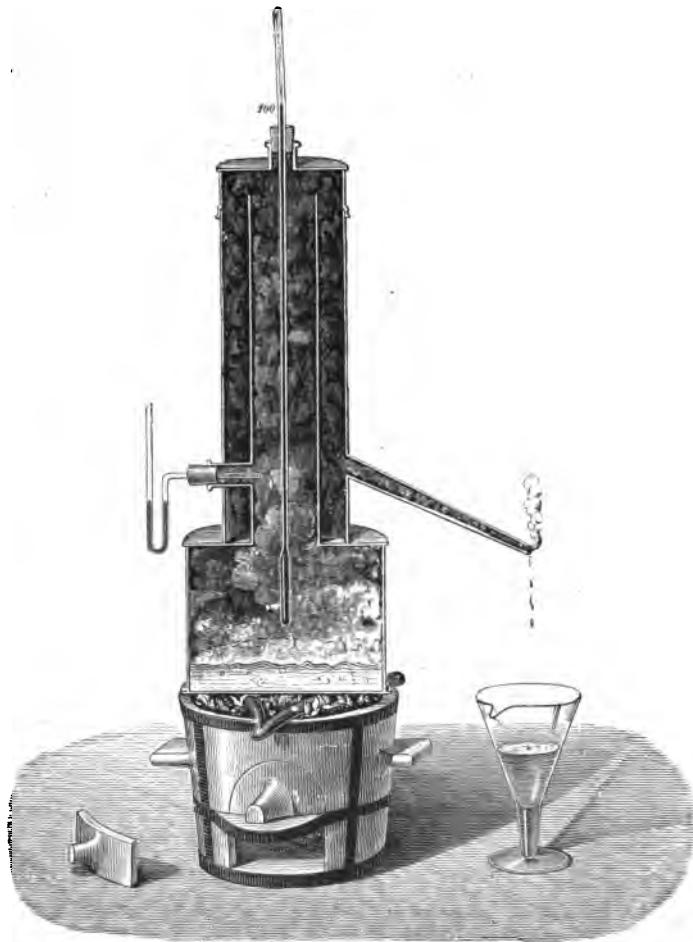


Fig. 8.—Determination of Boiling-point.

It has also been observed that if water be made to boil in an open metallic vessel, under average atmospheric pressure (76 centimetres, or 29.922 inches), and if the thermometer be plunged into the steam, the mercury stands at the same point during the entire time of ebullition, provided that the external pressure does not change. This second fixed temperature is called  $100^{\circ}$  in the Centigrade scale (whence

the name), and  $212^{\circ}$  on Fahrenheit's scale. In order to mark this second point on the thermometer, an apparatus is employed which was devised by Gay-Lussac, and perfected by Regnault. It consists of a copper boiler (Fig. 8) containing water which is raised to ebullition by means of a furnace. The steam circulates through a double casing, and escapes by a tube near the bottom. The thermometer is fixed in the interior casing, and when the mercury has become stationary, a mark is made at the point at which it stops, which denotes what is commonly called for brevity the *boiling-point*.

A small manometric tube, open at both ends, serves to show, by the equality of level of the mercury in its two branches, that the ebullition is taking place at a pressure equal to that which prevails externally, and consequently that the steam is escaping with sufficient freedom. It frequently happens that the external pressure is not exactly 760 millimetres, in which case the boiling-point should be placed a little above or a little below the point at which the mercury remains stationary, according as the pressure is less or greater than this standard pressure. When the difference on either side is inconsiderable, the position of the boiling-point may be roughly calculated by the rule, that a difference of 27 millimetres in the pressure causes a difference of  $1^{\circ}$  in the temperature of the steam produced. We shall return to this point in Chap. ix.

It now only remains to divide the portion of the instrument between the freezing and boiling points into equal parts corresponding to single degrees, and to continue the division beyond the fixed points. Below the zero point are marked the numbers 1, 2, 3, &c. These temperatures are expressed with the sign —. Thus the temperature of  $17^{\circ}$  below zero is written — $17^{\circ}$ .

**7. Adjustment of the Quantity of Mercury.**—In order to avoid complicating the above explanation, we have omitted to consider an operation of great importance, which should precede those which we have just described. This is the determination of the volume which

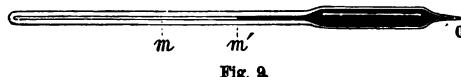


Fig. 2

must be given to the reservoir, in order that the instrument may have the required range. When the reservoir is cylindrical, this is easily effected in the following manner. Suppose we wish the thermometer to indicate temperatures comprised between  $-20^{\circ}$  and  $130^{\circ}$  Cent., so that the range is to be  $150^{\circ}$ ; the reservoir is left open at O (Fig. 9),

and is filled through this opening, which is then hermetically sealed. The instrument is then immersed in two baths whose temperatures differ, say, by  $50^{\circ}$ , and the mercury rises through a distance  $m m'$ . This length, if the quantity of mercury in the reservoir be exactly sufficient, should be the third part of the length of the stem. The quantity of mercury in the reservoir is always taken too large at first, so that it has only to be reduced, and thus the space traversed by the liquid is at first too great. Suppose it to be equal to  $\frac{4}{3}$ ths of the length of the stem. The degrees will then be too long, in the ratio  $\frac{3}{4} : \frac{1}{3} = \frac{9}{4}$ ; that is, the reservoir is  $\frac{9}{4}$  of what it should be. We therefore measure off  $\frac{4}{3}$ ths of the length of the reservoir, beginning at the end next the stem; this distance is marked by a line, and the end O is then broken and the mercury suffered to escape. The glass is then melted down to the marked line, and the reservoir is thus brought to the proper dimensions. It only remains to regulate the quantity of mercury admitted, by making it fill the tube at the highest temperature which the instrument is intended to indicate.

If the reservoir were spherical, which is a shape generally ill adapted for delicate thermometers, the foregoing process would be inapplicable, and it would be necessary to determine the proper size by trial.

**8. Thermometric Scales.**—In the *Centigrade* scale the freezing-point is marked  $0^{\circ}$ , and the boiling-point  $100^{\circ}$ . In *Réaumur's* scale, which is still popularly used on the Continent, the freezing-point is also marked  $0^{\circ}$ , but the boiling-point is marked  $80^{\circ}$ . Hence, 5 degrees on the former scale are equal to 4 on the latter, and the reduction of temperatures from one of these scales to the other can be effected by multiplying by  $\frac{4}{5}$  or  $\frac{5}{4}$ .

For example, the temperature  $75^{\circ}$  Centigrade is the same as  $60^{\circ}$  Réaumur, since  $75 \times \frac{4}{5} = 60$ ; and the temperature  $36^{\circ}$  Réaumur is the same as  $45^{\circ}$  Centigrade, since  $36 \times \frac{5}{4} = 45$ .

The relation between either of these scales and that of *Fahrenheit* is rather more complicated, inasmuch as *Fahrenheit's* zero is not at freezing-point, but at 32 of his degrees below it.



Fig. 10.  
Thermometric Scales.

As regards intervals of temperature, 180 degrees Fahrenheit are equal to 100 Centigrade, or to 80 Réaumur, and hence, in lower terms, 9 degrees Fahrenheit are equal to 5 Centigrade, or to 4 Réaumur.

The conversion of temperatures themselves (as distinguished from intervals of temperature) will be best explained by a few examples.

**Example 1.** To find what temperatures on the other two scales are equivalent to the temperature 50° Fahrenheit.

Subtracting 32, we see that this temperature is 18 Fahrenheit degrees above freezing-point, and as this interval is equivalent to  $18 \times \frac{5}{9}$ , that is 10 Centigrade degrees, or to  $18 \times \frac{4}{9}$ , that is 8 Réaumur degrees, the equivalent temperatures are respectively 10° Centigrade and 8° Réaumur.

**Example 2.** To find the degree on Fahrenheit's scale, which is equivalent to the temperature 25° Centigrade.

An interval of 25 Centigrade degrees is equal to  $25 \times \frac{9}{5}$ , that is 45 Fahrenheit degrees, and the temperature in question is above freezing-point by this amount. The number denoting it on Fahrenheit's scale is therefore  $32 + 45$ , that is 77°.

The rules for the conversion of the three thermometric scales may be summed up in the following formulæ, in which F, C, and R denote equivalent temperatures expressed in degrees of the three scales:—

$$F = \frac{9}{5} C + 32 = \frac{9}{5} R + 32.$$

$$C = \frac{5}{9} R = \frac{5}{9} (F - 32).$$

$$R = \frac{5}{9} C = \frac{5}{9} (F - 32).$$

It is usual, in stating temperatures, to indicate the scale referred to by the abbreviations *Fahr.*, *Cent.*, *Réau.*, or more briefly by the initial letters F., C., R.

**9. Displacement of the Zero Point.**—A thermometer left to itself after being made, gradually undergoes a contraction of the bulb, leading to a uniform error of excess in its indications. This phenomenon is attributable to molecular change in the glass, which has, so to speak, been tempered in the construction of the instrument, and to atmospheric pressure on the exterior of the bulb, which is resisted by the internal vacuum. The change is most rapid at first, and usually becomes insensible after a year or so, unless the thermometer is subjected to extreme temperatures. Its total amount is usually about half a degree. On account of this change it is advisable not to graduate a thermometer till some time after it has been sealed.

**10. Sensibility of the Thermometer.**—The power of the instrument to detect very small differences of temperature may be regarded as measured by the length of the degrees, which is proportional to the capacity of the bulb directly and to the section of the tube inversely (§ 24).

Quickness of action, on the other hand, requires that the bulb be small in at least one of its dimensions, so that no part of the mercury shall be far removed from the exterior, and also that the glass of the bulb be thin.

Quickness of action is important in measuring temperatures which vary rapidly. It should also be observed that, as the thermometer, in coming to the temperature of any body, necessarily causes an inverse change in the temperature of that body, it follows that when the mass of the body to be investigated is very small, the thermometer itself should be of extremely small dimensions, in order that it may not cause a sensible variation in the temperature which is to be observed.

**11. Alcohol Thermometer.**—In the construction of thermometers, other liquids may be introduced instead of mercury; and alcohol is very frequently employed for this purpose.

Alcohol has the disadvantage of being slower in its action than mercury, on account of its inferior conductivity; but it can be employed for lower temperatures than mercury, as the latter congeals at  $-39^{\circ}$  Cent. ( $-38^{\circ}$  Fahr.), whereas the former has never congealed at any temperature yet attained.

If an alcohol thermometer is so graduated as to make it agree with a mercurial thermometer (which is the usual practice), its degrees will not be of equal length, but will become longer as we ascend on the scale. If mercury is regarded as expanding equally at all temperatures, alcohol must be described as expanding more at high than at low temperatures.

**12. Self-registering Thermometers.**—It is often important for meteorological purposes to have the means of knowing the highest or the lowest temperature that occurs during a given interval. Instruments intended for this purpose are called maximum and minimum thermometers.

The oldest instrument of this class is *Six's* (Fig. 11), which is at once a maximum and a minimum thermometer. It has a large cylindrical bulb C filled with alcohol, which also occupies a portion of the tube. The remainder of the tube is partly filled with mercury,

which occupies a portion of the tube shaped like the letter U, one extremity of the mercurial column being in contact with the alcohol already mentioned, while the other extremity is in contact with a second column of alcohol; and beyond this there is a small space occupied only with air, so as to leave room for the expansion of the liquids.

When the alcohol in the bulb expands, it pushes the mercurial column before it, and when it contracts the mercurial column follows it. The extreme points reached by the two ends of the mercurial column are registered by a pair of light steel indices  $c$ ,  $d$  (shown on an enlarged scale at K), which are pushed before the ends of the column, and then are held in their places by springs, which are just strong enough to prevent slipping, so that the indices do not follow the mercury in its retreat. One of the indices  $d$  registers the maximum and the other  $c$  the minimum temperature which has occurred since the instrument was last set. The setting consists in bringing the indices into contact with the ends of the mercurial column, and is usually effected by means of a magnet. This instrument is now, on account of its complexity, little used. It possesses, however, the advantages of being equally quick (or slow) in its action for maximum and minimum temperatures, which is an important property when these temperatures are made the foundation for the computation of the mean temperature of the interval, and of being better able than most of the self-registering thermometers to bear slight jolts without disturbance of the indices.

*Rutherford's* self-registering thermometers are frequently mounted together on one frame, as in Fig. 12, but are nevertheless distinct instruments. His *minimum* thermometer, which is the only minimum thermometer in general use, has alcohol for its fluid, and is always placed with its tube horizontal, or nearly so. In the fluid column there is a small index  $n$  of glass or enamel, shaped like a dumb-bell.

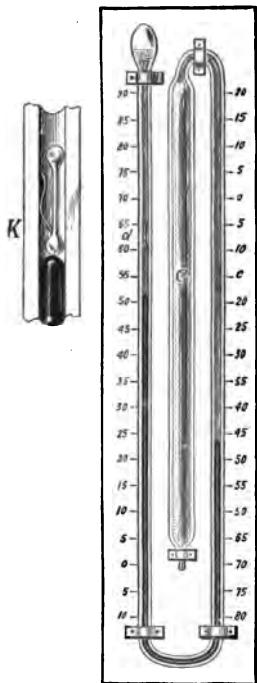


Fig. 11.—Six's Self-registering Thermometer.

When contraction occurs, the index, being wetted by the liquid, is drawn backwards by the contractile force of the liquid surface (see *Capillarity* in Part I.); but when expansion takes place the index remains stationary in the interior of the liquid. Hence the minimum temperature is indicated by the position of the

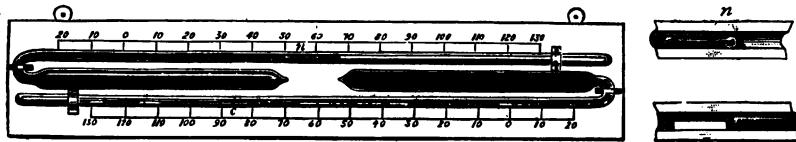


Fig. 12.—Rutherford's Maximum and Minimum Thermometers.

forward end of the index. The instrument is set by inclining it so as to let the index slide down to the end of the liquid column.

The only way in which this instrument is liable to derangement is by a portion of the spirit evaporating from the column and becoming condensed in the end of the tube, which usually terminates in a small bulb. When the portion thus detached is large, or when the column of spirit becomes broken into detached portions by rough usage in travelling, "let the thermometer be taken in the hand by the end farthest from the bulb, raised above the head, and then forcibly swung down towards the feet; the object being, on the principle of centrifugal force, to send down the detached portion of spirit till it unites with the column. A few throws or swinging strokes will generally be sufficient; after which the thermometer should be placed in a slanting position, to allow the rest of the spirit still adhering to the sides of the tube to drain down to the column. But another method must be adopted if the portion of spirit in the top of the tube be small. Heat should then be applied slowly and cautiously to the end of the tube where the detached portion of spirit is lodged; this being turned into vapour by the heat will condense on the surface of the unbroken column of spirit. Care should be taken that the heat is not too quickly applied. . . . The best and safest way to apply the requisite amount of heat, is to bring the end of the tube slowly down towards a minute flame from a gas-burner; or if gas is not to be had, a piece of heated metal will serve instead."<sup>1</sup>

Rutherford's *maximum* thermometer is a mercurial thermometer, with the stem placed horizontally, and with a steel index *c* in the tube, outside the mercurial column. When expansion occurs, the

<sup>1</sup> Buchan's *Handy Book of Meteorology*, p. 62.

index, not being wetted by the liquid, is forced forwards by the contractile force of the liquid surface (see *Capillarity* in Part I.); but when contraction takes place, the index remains stationary outside the liquid. Hence the maximum temperature is indicated by the position of the backward end of the index. The instrument is set by bringing the index into contact with the end of the liquid column, an operation which is usually effected by means of a magnet.

This thermometer is liable to get out of order after a few years' use, by chemical action upon the surface of the index, which causes it to become wetted by the mercury, and thus renders the instrument useless.

*Phillips'* maximum thermometer (invented by Professor Phillips, the eminent geologist, and made by Casella) is recommended for use in the official *Instructions for Taking Meteorological Observations*, drawn up by Sir Henry James for the use of the Royal Engineers. It is a mercurial thermometer not deprived of air. It has an exceed-

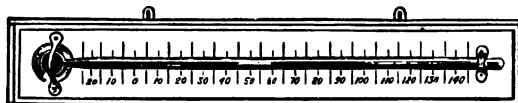


Fig. 13.—Phillips' Maximum Thermometer.

ingly fine bore, and the mercurial column is broken by the insertion of a small portion of air. The instrument is set by reducing this portion of air to the smallest dimensions which it can be made to assume, and is placed in a horizontal position. When the mercury expands, it pushes forwards this intervening air and the detached column of mercury beyond it; but when contraction takes place the intervening air expands, and the detached column remains unmoved.

The detached column is not easily shaken out of its place, and when the bore of the tube is made sufficiently narrow the instrument may even be used in a vertical position, a property which is often of great service.

In Negretti and Zambra's maximum thermometer (Fig. 14), which is employed at the Royal Observatory, Greenwich, there is an obstruction in the bent part of the tube, near the bulb, which barely leaves room for the mercury to pass when forced up by expansion, and is sufficient to prevent it from returning when the bulb cools.

The objection chiefly urged against this thermometer is the extreme mobility of the detached column, which renders it very liable to



Fig. 14.—Negretti's Maximum Thermometer.

accidental displacement; but in the hands of a skilful observer this is of no moment. Dr. Balfour Stewart (*Elementary Treatise on Heat*, p. 20, 21), says:—"When used, the stem of this instrument ought to be inclined downwards. . . . It does not matter if the column past the obstruction go down to the bottom of the tube; for when the instrument is read, it is gently tilted up until this detached column flows back to the obstruction, where it is arrested, and the end of the column will then denote the maximum temperature. In resetting the instrument, it is necessary to shake the detached column past the obstruction in order to fill up the vacancy left by the contraction of the fluid after the maximum had been reached."

**DEEP-SEA AND WELL THERMOMETERS.**—Self-registering thermometers intended for observing at great depths in water should be inclosed in an outer case of glass hermetically sealed, the intervening space being occupied wholly or partly by air, so that the pressure outside may not be transmitted to the thermometer. A thermometer not thus protected gives too high a reading, because the compression of the bulb forces the liquid up the tube. The instrument represented in Fig. 15 was designed by Lord Kelvin for the Committee on Underground Temperature appointed by the British Association. A is the protecting case, B the Phillips' thermometer inclosed in it, and supported by three pieces of cork *ccc.* A small quantity of spirit *s* occupies the lower part of the case; *d* is the air-bubble characteristic of Phillips' thermometer, and serving to separate one portion of the mercurial column from the rest. In the figure this air-bubble is represented as expanded by the descent of the lower portion of mercury, while the upper portion remains suspended by adhesion. This instrument has been found to register correctly even under a pressure of  $2\frac{1}{2}$  tons to the square inch.



Fig. 15.  
Thomson's  
Protected  
Thermometer.

The use of the spirit *s* is to bring the bulb more quickly to the temperature of the surrounding medium.

Another instrument, designed, like the foregoing, for observations in wells and borings, is *Walferdin's maximum thermometer* (Fig. 16). Its tube terminates above in a fine point opening into a cavity of considerable size, which contains a sufficient quantity of mercury to cover the point when the instrument is inverted. The instrument is set by placing it in this inverted position and warming the bulb until the mercury in the stem reaches the point and becomes connected with the mercury in the cavity. The bulb is then cooled to a temperature lower than that which is to be observed; and during the operation of cooling, mercury enters the tube so as always to keep it full. The instrument is then lowered in the erect position into the bore where observations are to be made, and when the temperature of the mercury rises a portion of it overflows from the tube. To ascertain the maximum temperature which has been experienced, the instrument may be immersed in a bath of known temperature, less than that of the boring, and the amount of void space in the upper part of the tube will indicate the excess of the maximum temperature experienced above that of the bath.

 Fig. 16. If the tube is not graduated, the maximum temperature can be ascertained by gradually raising the temperature of the bath till the tube is just full.

If the tube is graduated, the graduations can in strictness only indicate true degrees for some one standard temperature of setting, since the length of a true degree is proportional to the quantity of mercury in the bulb and tube; but a difference of a few degrees in the temperature of setting is immaterial, since  $10^{\circ}$  Cent. would only alter the length of a degree by about one six-hundredth part.

**13. Thermograph.**—A continuous automatic record of the indications of a thermometer can be obtained by means of photography, and this plan is now adopted at numerous observatories. The following description relates to the Royal Observatory, Greenwich. A sheet of sensitized paper is mounted on a vertical cylinder just behind the mercurial column, which is also vertical, and is protected from the action of light by a cover of blackened zinc, with the exception of a narrow vertical strip just behind the mercurial column. A strong beam of light from a lamp or gas flame is concentrated by a cylindric

lens, so that if the thermometer were empty of mercury a bright vertical line of light would be thrown on the paper. As this beam of light is intercepted by the mercury in the tube, which for this purpose is made broad and flat, only the portion of the paper above the top of the mercurial column receives the light, and is photographically affected. The cylinder is made to revolve slowly by clock-work, and if the mercury stood always at the same height, the boundary between the discoloured and the unaffected parts of the paper would be straight and horizontal, in consequence of the horizontal motion of the paper itself. In reality, the rising and falling of the mercury, combined with the horizontal motion of the paper, causes the line of separation to be curved or wavy, and the height of the curve above a certain datum-line is a measure of the temperature at each instant of the day.<sup>1</sup> The whole apparatus is called a *thermograph*, and apparatus of a similar character is employed for obtaining a continuous photographic record of the indications of the barometer<sup>2</sup> and magnetic instruments.

**14. Metallic Thermometers.**—Thermometers have sometimes been constructed of solid metals. Breguet's thermometer, for example (Fig. 17), consists of a helix carrying at its lower end a horizontal needle which traverses a dial. The helix is composed of three metallic strips, of silver, gold, and platinum, soldered together so as to form a single ribbon. The silver, which is the most expansible, is placed in the interior of the helix; the platinum, which is the least expansible, on the exterior; and the gold serves to connect them. When the temperature rises, the helix unwinds and produces a deflection of the needle; when the temperature falls, the helix winds up and deflects the needle in the opposite direction.

Fig. 18 represents another dial-thermometer, in which the thermometric portion is a double strip composed of steel and brass, bent into the form of a nearly complete circle, as shown by the dotted lines in the figure. One extremity is fixed, the other is jointed to the

<sup>1</sup> Strictly speaking, the temperatures corresponding to the various points of the curve are not read off by reference to a single datum-line, but to a number of datum-lines which represent the shadows of a set of horizontal wires stretched across the tube of the thermometer at each degree, a broader wire being placed at the decades, and also at 32°, 52°, and 72°.

In order to give long degrees, the bulb of the thermometer is made very large—eight inches long, and  $\frac{1}{4}$  of an inch in internal diameter.—(*Greenwich Observations*, 1847.)

<sup>2</sup> See *Photographic Registration* in Part I.

shorter arm of a lever, whose longer arm carries a toothed sector. This latter works into a pinion, to which the needle is attached.

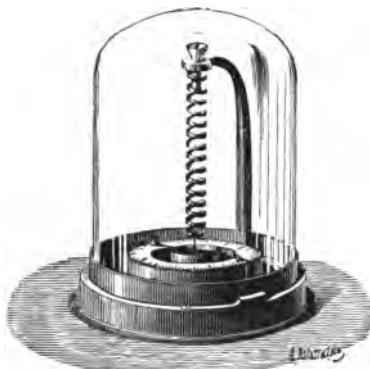


Fig. 17.—Breguet's Thermometer.



Fig. 18.—Metallic Thermometer.

Immisch's thermometer, which is extremely portable and convenient, contains a crescent-shaped thin metallic vessel (Fig. 19) filled with a highly expansive liquid. With rise of temperature, the horns A B of the crescent are further separated by the expansive force of the liquid, and the movement is transmitted to a hand which travels round a dial.

It may be remarked that dial-thermometers are very well adapted for indicating maximum and minimum temperatures, it being only

necessary to place on opposite sides of the needle a pair of movable indices, which could be pushed in either direction according to the variations of temperature.

Generally speaking, metallic thermometers offer great facilities for automatic registration.

In Secchi's meteorograph, for example, the temperature is indicated and registered by the expansion of a long strip of brass (about 17 metres long) kept constantly stretched by a suitable weight; this expansion is rendered sensible by a system of levers connected with the tracing point. The thermograph of Hasler and Escher consists of a steel and a brass band connected together and rolled into the form of a spiral. The movable extremity of the spiral, by acting upon a projecting arm, produces rotation of a steel axis which carries the tracer.

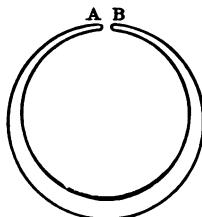


Fig. 19.

**15. Pyrometers.**—Metallic thermometers can generally be employed for measuring higher temperatures than a mercurial thermometer could bear; but there is great difficulty in constructing any instrument to measure temperatures as high as those of furnaces. Instruments intended for this purpose are called pyrometers.

Wedgwood, the famous potter, invented an apparatus of this kind, consisting of a gauge for measuring the contraction experienced by a piece of baked clay when

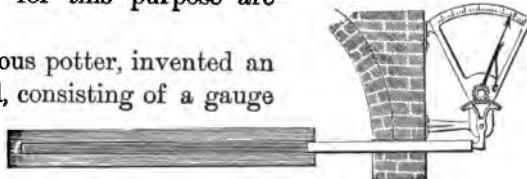


Fig. 20.—Brongniart's Pyrometer.

placed in a furnace; and Brongniart introduced into the porcelain manufactory at Sèvres the instrument represented in Fig. 20, consisting of an iron bar lying in a groove in a porcelain slab, with one end abutting against the bottom of the groove, and the other projecting through the side of the furnace, where it gave motion to an indicator.

Neither of these instruments has, however, been found to furnish consistent indications, and the only instrument that is now relied on for the measurement of very high temperatures is the air-thermometer.

Of late years much attention has been given to the measurement of temperature by an electrical method depending on the fact that the resistance of a metal to the passage of a current of electricity increases with the temperature. Platinum is the metal usually selected for this purpose, and the instrument employed is called the *platinum pyrometer*, or the *electrical pyrometer*.

**16. Differential Thermometer.**—Leslie of Edinburgh invented, in the beginning of the present century, the instrument shown in Fig. 21, for detecting small differences of temperature. A column of sulphuric acid, coloured red, stands in the two branches of a bent tube, the extremities of which terminate in two equal bulbs containing air. When both globes are at the same temperature, whatever that temperature may be, the liquid, if the instrument is in order, stands at the same height in both branches. This height is marked zero on both scales. When there is a difference of temperature between them, the expansion of the air in the warmer bulb produces a depression of the liquid on that side and an equal elevation on the other side.

The differential thermometer is an instrument of great sensibility, and enabled Leslie to conduct some important investigations on the subject of the radiation of heat. It is now, however, superseded by the thermo-pile invented by Melloni. This latter instrument will be

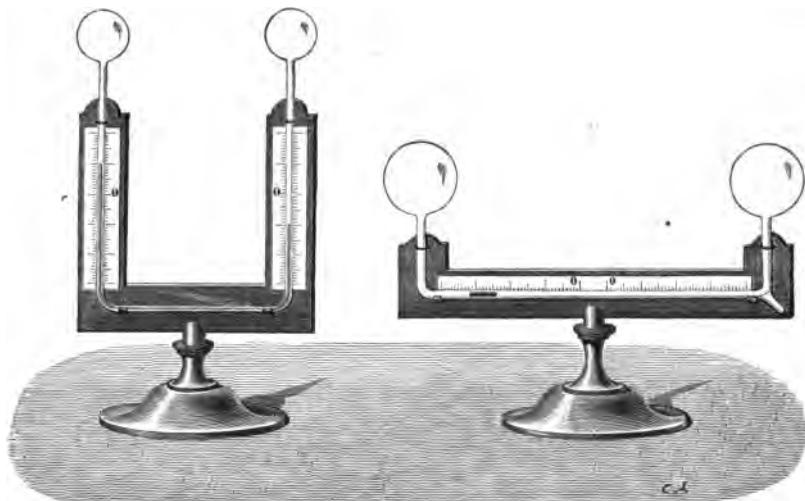


Fig. 21.—Leslie's Differential Thermometer.

Fig. 22.—Rumford's Thermoscope.

described in another portion of this work. Rumford's thermoscope (Fig. 22) is analogous to Leslie's differential thermometer. It differs from it in having the horizontal part much longer, and the vertical branches shorter. In the horizontal tube is an alcohol index, which, when the two globes are at the same temperature, occupies exactly the middle.

## CHAPTER II.

### MATHEMATICS OF EXPANSION.

17. **Expansion. Factor of Expansion.**—When a body expands from volume  $V$  to volume  $V+v$ , the ratio  $\frac{v}{V}$  is called the *expansion of volume* or the *cubical expansion* of the body.

In like manner if the length, breadth, or thickness of a body increases from  $L$  to  $L+l$ , the ratio  $\frac{l}{L}$  is called the *linear expansion*.

The ratio  $\frac{V+v}{V}$  will be called, in this treatise, the *factor of cubical expansion*, and the ratio  $\frac{L+l}{L}$  the *factor of linear expansion*. In each case the factor of expansion is *unity plus the expansion*.

Similar definitions apply to expansion of area or superficial expansion; but it is seldom necessary to consider this element in thermal discussions.

18. **Relation between Linear and Cubical Expansion.**—If a cube, whose edge is the unit length, expands equally in all directions, the length of each edge will become  $1+l$ , where  $l$  is the linear expansion; and the volume of the cube will become  $(1+l)^3$  or  $1+3l+3l^2+l^3$ .

In the case of the thermal expansion of solid bodies  $l$  is always very small, so that  $l^2$  and  $l^3$  can be neglected, and the expansion of volume is therefore  $3l$ ; that is to say, the *cubical expansion is three times the linear expansion*. This is illustrated geometrically by Fig. 23, which represents a unit cube with a plate of thickness  $l$  and therefore of volume  $l$  applied to each of three faces; the total volume added being therefore  $3l$ .

Similar reasoning shows that the *superficial expansion is double the linear expansion*.

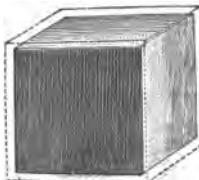


Fig. 23.

These results have been deduced from the supposition of equal expansion in all directions. If the expansions of the cube in the directions of three conterminous edges be denoted by  $a, b, c$ , the angles being supposed to remain right angles, the volume will become  $(1+a)(1+b)(1+c)$  or  $1+a+b+c+ab+ac+bc+abc$ , which, when  $a, b$  and  $c$  are so small that their products can be neglected, becomes  $1+a+b+c$ ; so that the expansion of volume is the sum of the expansions of length, breadth, and thickness.

**19. Variation of Density.**—Since the density of a body varies inversely as its volume, the density after expansion will be obtained by dividing the original density by the factor of expansion. In fact, if  $V, D$  denote the volume and density before, and  $V', D'$  after expansion, the mass of the body, which remains unchanged, is equal to  $VD$ , and also to  $V'D'$ . We have therefore  $\frac{D'}{D} = \frac{V}{V'} = \frac{1}{1+\epsilon}$ , where  $\epsilon$  denotes the expansion of volume, and therefore  $1+\epsilon$  the factor of expansion.

Since  $\frac{1}{1+\epsilon}$  is  $1-\epsilon+\epsilon^2-\epsilon^3+\&c.$ , it is sensibly equal to  $1-\epsilon$  when  $\epsilon$  is small. We have therefore  $D' = D(1-\epsilon)$ .

**20. Real and Apparent Expansion.**—When the volume of a liquid is specified by the number of divisions which it occupies in a graduated vessel, it is necessary to take into account the expansion of the vessel, if we wish to determine the true expansion of the liquid.

Let  $a$  denote the apparent expansion computed by disregarding the expansion of the vessel and attending only to the number of divisions occupied. Then if  $n$  be the number of divisions occupied before, and  $n'$  after expansion, we have

$$n' = n(1+a).$$

Let  $g$  denote the real expansion of the containing vessel; then if  $d$  be the volume of each division before, and  $d'$  after expansion, we have

$$d' = d(1+g).$$

Let  $m$  denote the real expansion of the liquid. Then if  $v$  denote the real volume of the liquid before, and  $v'$  after expansion, we have

$$v' = v(1+m).$$

But since the volume  $v$  consists of  $n$  parts each having the volume  $d$ , we have

$$v = nd,$$

and in like manner

$$v' = n'd'.$$

Substituting for  $n'$  and  $d'$  in this last equation, we have

$$\nu' = n(1+a)d(1+g) = \nu(1+a)(1+g).$$

But  $\nu' = \nu(1+m)$ .

Hence we have

$$(1+a)(1+g) = 1+m;$$

that is, *the factor of real expansion of the liquid is the product of the factor of real expansion of the vessel and the factor of apparent expansion.* Multiplying out, we have

$$1+a+g+ag=1+m,$$

and as the term  $ag$ , being the product of two small quantities, is usually negligible, we have sensibly

$$a+g=m;$$

that is, the expansion of the liquid is the sum of the expansion of the glass and the apparent expansion.

This investigation is applicable to the mercurial thermometer when the capacity of the bulb has been expressed in degrees of the stem.

Similar reasoning applies to the apparent expansion of a bar of one metal as measured by means of a graduated bar of a less expandible metal. The real expansion of the bar to be measured will be sensibly equal to the sum of the expansion of the measuring bar and the apparent expansion.

In adopting the mercurial thermometer as the standard of temperature (the tube being graduated into equal parts), we virtually adopt the apparent expansion of mercury in glass as our standard of *uniform* expansion.

**21. Physical Meaning of the Degrees of the Mercurial Thermometer.** —Since the stem of a mercurial thermometer is divided into degrees of equal capacity, we can express the capacity of the bulb in degrees. Let the capacity of the bulb together with as much of the stem as is below the freezing-point be  $N$  degrees, and let the interval from freezing to boiling point be  $n$  degrees; then  $\frac{n}{N}$  is the apparent expansion of the mercury from freezing to boiling point. When the Centigrade scale is employed, this apparent expansion is  $\frac{100}{N}$ , and the apparent expansion from zero to  $t^{\circ}$  is  $\frac{t}{N}$ . Hence the apparent expansion from zero to  $t^{\circ}$  is  $\frac{t}{100}$  of the apparent expansion from zero to  $100^{\circ}$ . This last statement constitutes the definition of the temperature  $t^{\circ}$  when the mercurial thermometer is regarded as the standard.

**22. Comparability of Mercurial Thermometers.**—If two mercurial thermometers, each of them constructed so as to have its degrees rigorously equal in capacity, agree in their indications at all temperatures, the above investigation shows that the apparent expansions of the mercury in the two instruments must be exactly proportional. But we have shown in § 20 that the apparent expansion  $\alpha$  is equal to  $m-g$ ,  $m$  denoting the real expansion of the mercury, and  $g$  that of the glass. Mercury, being a liquid and an elementary substance, can always be obtained in the same condition, so that  $m$  will have the same value in the two thermometers; but it is difficult to ensure that two specimens of glass shall be exactly alike; hence  $g$  has different values in different thermometers. The agreement of the two thermometers does not, however, require identity in the values of  $m-g$ , but only proportionality; in other words it requires that the fraction

$$\frac{m-g_1}{m-g_2}$$

(where  $g_1$  and  $g_2$  are the values of  $g$  for the two instruments) shall have the same value at all temperatures.

The average value of  $g$  is about  $\frac{1}{7}$  of that of  $m$ . In other words mercury expands about 7 times as much as glass.

**23. Steadiness of Zero in Spirit Thermometers.**—It is obvious from § 21 that the volume of a degree can be computed by multiplying the capacity of the bulb by the number which denotes the apparent expansion for one degree. Alcohol expands about 6 times as much as mercury, and its apparent expansion in glass is about 7 times that of mercury. Hence with the same size of bulb, the degrees of an alcohol thermometer will be about 7 times as large as those of a mercurial thermometer, and a contraction of the bulb which produces a change of one degree in the reading of a mercurial thermometer, would only produce a change of one-seventh of a degree in the reading of an alcohol thermometer. This is the reason, or at all events one reason, why displacement of the zero point (§ 9) is insignificant in spirit thermometers.

**24. Length of a Degree on the Stem.**—Since the length of a degree upon the stem of a thermometer is equal to the volume of a degree divided by the sectional area of the tube, the formula for this length is  $\frac{\alpha C}{\pi}$ , where  $\alpha$  denotes the apparent expansion for one degree,  $C$  the capacity of the bulb with as much of the stem as is below zero, and

$s$  the sectional area of the stem. The value of  $\alpha$  for the mercurial Centigrade thermometer is about  $\frac{1}{6480}$ .

**25. Weight Thermometer.**—In the weight thermometer (Fig. 24) the apparent expansion of mercury is observed by comparing the weight of the mercury which passes the zero point with that of the mercury which remains below it. The tube is open, and its mouth is the zero point. The instrument is first filled with mercury at zero, and is then exposed to the temperature which it is required to measure. The mercury which overflows is caught and weighed, and the weight of the mercury which remains in the instrument is also determined—usually by subtracting the weight of the overflow from that of the original contents. The weight of the overflow, divided by the weight of what remains, is equal to the apparent expansion; for it is the same as the ratio of the volume of mercury above the zero point to the volume below it in an ordinary thermometer.

In order to measure temperatures in degrees, with this thermometer, the apparent expansion from  $0^\circ$  to  $100^\circ$  C. must be determined once for all and put on record. One hundredth part of this must be divided into the apparent expansion observed at the unknown temperature  $t^\circ$ , and the quotient will be  $t$ .

**26. Expansion of Gases.**—In the case of solids and liquids the expansions produced by heat are usually very small, so that it is not important to distinguish between the value of  $\frac{v}{V}$  and the value of  $\frac{v}{V+v}$  (§ 17). But in the case of gases much larger expansions occur, and it is essential to attend to the above distinction. By general agreement, the volume of a gas at zero (Centigrade) is taken as the standard with which the volume at any other temperature is to be compared. We shall denote the volume at zero by  $V_0$ , and the volume at temperature  $t^\circ$  by  $V_t$ . Then, if the pressure be the same at both temperatures, we shall write

$$V_t = V_0 (1 + \alpha t)$$

where  $\alpha$  is called the mean coefficient of expansion between the temperatures  $0^\circ$  and  $t^\circ$ . Experiment has shown that when temperatures are measured by the mercurial thermometer, graduated in the manner which we have already described,  $\alpha$  is practically the same at all temperatures which lie within the range of the mercurial



Fig. 24.  
Weight Ther-  
mometer.

thermometer. In other words, the expansions of gases are sensibly proportional to the apparent expansion of mercury in glass. Moreover, the coefficient  $\alpha$  is not only the same for different temperatures, but it is also the same for different gases; its value being always very approximately

$$\cdot 00366 \text{ or } \frac{1}{273}.$$

By Boyle's law, the product of the volume and pressure of a gas remains constant when the temperature is constant. We have been supposing the pressure to remain constant, so that the product in question is proportional to the volume only. If the volume is kept constant the pressure will vary in proportion to  $1 + \alpha t$ , so that we shall have

$$P_t = P_0 (1 + \alpha t),$$

$P_0$  and  $P_t$  denoting the pressures at  $0^\circ$  and  $t^\circ$  respectively. If we remove all restriction, we have

$$(VP)_t = (VP)_0 (1 + \alpha t),$$

where  $(VP)_0$ ,  $(VP)_t$  denote the products of volume and pressure at  $0^\circ$  and  $t^\circ$  respectively. Hence the value of the expression

$$\frac{VP}{1 + \alpha t}$$

will be the same for all values of  $V$ ,  $P$  and  $t$ . Since the mass is unchanged, the density  $D$  varies inversely as the volume, and therefore

$$\frac{P}{D(1 + \alpha t)}$$

is also constant.

**27. General Definition of Coefficient of Expansion.**—If  $V_0$  denote the volume of any substance at temperature  $0^\circ$  (Centigrade),  $V_t$  its volume under the same pressure at temperature  $t^\circ$ , and  $V_{t'}$  its volume at a higher temperature  $t'$ , the *mean coefficient of expansion*  $\alpha$  between the temperatures  $t$  and  $t'$  is defined by the equation

$$V_{t'} - V_t = V_0 \alpha (t' - t),$$

and the *coefficient of expansion at the temperature  $t^\circ$*  is the limit to which  $\alpha$  approaches as  $t'$  approaches  $t$ ; that is, in the language of the differential calculus, it is

$$\frac{1}{V_0} \frac{dV}{dt}.$$

If we make  $V_0$  unity, the coefficient of expansion at temperature  $t$  will be simply

$$\frac{dV}{dt}.$$

## CHAPTER III.

### EXPANSION OF SOLIDS.

28. **Observations of Linear Expansion.**—Laplace and Lavoisier determined the linear expansion of a great number of solids by the following method.

The bar AB (Fig. 25) whose expansion is to be determined, has one end fixed at A, while the other can move freely, pushing before it the lever OB, which is movable about the point O, and carries a telescope whose line of sight is directed to a scale at some distance. A displacement BB' corresponds to a considerably greater length CC' on the scale, the ratio of the former to the latter being the same as that of OB to OC.

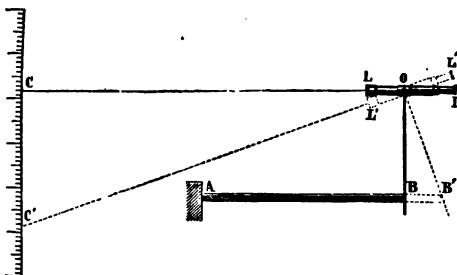


Fig. 25.  
Principle of the Method of Laplace and Lavoisier.

The apparatus employed by Laplace and Lavoisier is shown in Fig. 26. The trough C, in which is laid the bar whose expansion is to be determined, is placed between four massive uprights of hewn stone N. One of the extremities of the bar rests against a fixed bar B', firmly joined to two of the uprights; the other extremity, which rests upon a roller to give it greater freedom of movement, pushes the bar B, which produces the rotation of the axis aa'. This axis carries with it in its rotation the telescope LL', which is directed to the scale. The first step is to surround the bar with melting ice, and take a reading through the telescope when the bar is at the temperature zero. The temperature of the trough is then raised, and read-

ings are taken, which, by comparison with the first, give the increase of length.

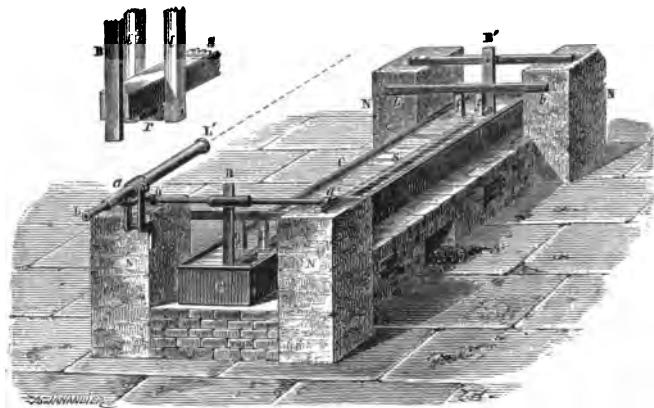


Fig. 26.—Apparatus of Laplace and Lavoisier.

The following table contains the most important results thus obtained:—

COEFFICIENTS OF LINEAR EXPANSION.

Gold, Paris standard, annealed, 0·000015153	Soft wrought iron, . . . . .	0·000012204
" " unannealed, 0·000015515	Round iron, wire drawn, . .	0·000012350
Steel not tempered, . . . . .	English flint-glass, . . . . .	0·000008116
Tempered steel reheated to 65°, 0·000012395	Gold, procured by parting, .	0·000014660
Silver obtained by cupellation, 0·000019075	Platina, . . . . .	0·000009918
Silver, Paris standard, . . . . .	Lead, . . . . .	0·0000088488
Copper, . . . . .	French glass with lead, . .	0·000008715
Brass, . . . . .	Sheet zinc, . . . . .	0·000029416
Malacca tin, . . . . .	Forged zinc, . . . . .	0·000031083
Falmouth tin, . . . . .		

The coefficient of expansion of a metal is not precisely the same at all temperatures, but it is sensibly constant from 0° to 100° C.

A simpler and probably more accurate method of observing expansions was employed by Ramsden and Roy. It consists in the direct observation of the distances moved by the ends of the bar, by means of two microscopes furnished with micrometers, the microscopes themselves being attached to an apparatus which is kept at a constant temperature by means of ice.

**29. Compensated Pendulum.**—The rate of a clock is regulated by the motion of its pendulum. Suppose the clock to keep correct time at a certain temperature. Then at higher temperatures the pendulum will be too long and will therefore vibrate too slowly, so that

the clock will lose. At lower temperatures, on the other hand, the clock will gain. To obviate or, at least, diminish this source of irregularity, the following methods of compensation are employed.

1. *Harrison's Gridiron Pendulum*.—This consists of four oblong frames, the uprights of which are alternately of steel F and of brass

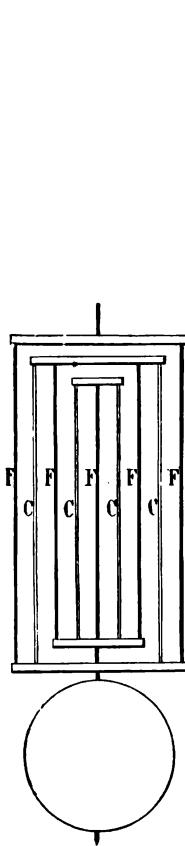


Fig. 27.  
Plan of Gridiron Pendulum.

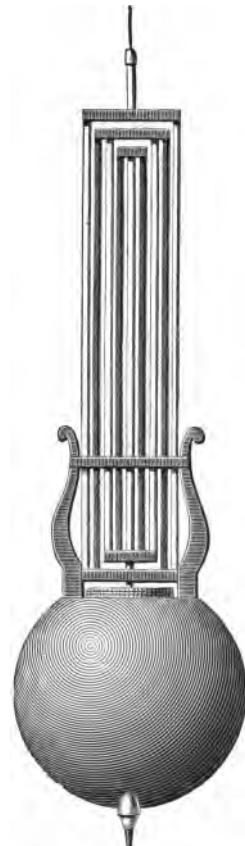


Fig. 28.  
Gridiron Pendulum.



Fig. 29.  
Graham's Mercurial Pendulum.

C (Fig. 27), so arranged that the bob will rise or fall through a distance equal to the difference between the total expansion of 3 steel rods and that of 2 brass rods. As the coefficients of expansion of these metals are nearly as 2 to 3, it is possible to make the compensation nearly exact.

2. *Graham's Mercurial Pendulum*.—This consists of an iron rod

carrying at its lower end a frame, in which are fixed one or two glass cylinders containing mercury. When the temperature rises, the lengthening of the rod lowers the centre of gravity and centre of oscillation of the whole; but the expansion of the mercury produces the contrary effect; and if there is exactly the right quantity of mercury the compensation will be nearly perfect.

**30. Force of Expansion of Solids.**--The *force of expansion* is often very considerable, being equal to the force necessary to compress the body to its original dimensions. Thus, for instance, iron when heated from  $0^{\circ}$  to  $100^{\circ}$  increases by .0012 of its original length. In order to produce a corresponding change of length in a rod an inch square by mechanical means, a force of about 15 tons would be required. This is accordingly the force necessary to prevent such a rod from expanding or contracting when heated or cooled through  $100^{\circ}$ .

This force has frequently been utilized for bringing in the walls of a building when they have settled outwards. For this purpose the walls are first tied together by iron rods, which pass through the walls, and are furnished at the ends with screws and nuts. All the nuts having been tightened against the wall, alternate bars are heated; and while they are hot, the nuts upon them, which have been thrust away from the wall by the expansion, are screwed home. As these bars cool, they draw the walls in and allow the nuts on the other bars to be tightened. The same operation is then repeated as often as may be necessary.

Iron cannot with safety be used in structures, unless opportunity is given it to expand and contract without doing damage. In laying a railway, small spaces must be left between the ends of the rails to leave room for expansion; and when sheets of lead or zinc are employed for roofing, room must be left for them to overlap.

## CHAPTER IV.

### EXPANSION OF LIQUIDS.

31. **Method of Equilibrating Columns.**—Most of the methods employed for measuring the expansion of liquids depend upon a previous knowledge of the expansion of glass, the observation itself consisting in a determination of the apparent expansion of the liquid relative to glass. There is, however, one method which is not liable to this objection, and it has been employed by Dulong and Petit, and afterwards by Regnault, for measuring the expansion of mercury—an element of great importance for many physical applications. It depends upon the hydrostatic principle that the heights of two liquid columns which produce equal pressures are inversely as their densities.

Let A and B (Fig. 30) be two tubes containing mercury, and communicating with each other by a very narrow horizontal tube CD at the bottom. If the temperature of the liquid be uniform, the mercury will stand at the same height in both branches; but if one column be kept at  $0^{\circ}$  and the other be heated, their densities will be unequal. Let  $d d'$  be their densities, and  $h h'$  their heights. Then since their pressures at the bottom are equal, we must have

$$hd = h'd'.$$

But if  $v$  and  $v'$  denote the volumes of one and the same mass of liquid at the two temperatures, we have

$$vd = v'd'.$$

From these two equations, we have

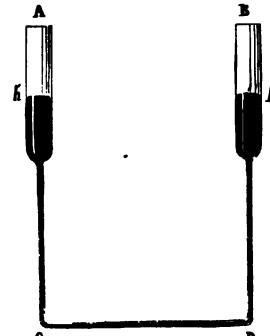


Fig. 30.  
Principle of Dulong's Method.

$$\nu : \sigma :: h : h'$$

so that the expansion of volume is directly given by a comparison of the heights. Denoting this expansion by  $m$ , we shall have

$$m = \frac{h' - h}{h}$$

Strictly speaking, the mercury in this experiment is not in equilibrium. There will be two very slow currents through the horizontal tube, the current from hot to cold being above, and the current from cold to hot below. Equilibrium of pressure will exist only at the intermediate level—that of the axis of the tube, and it is from this level that  $h$  and  $h'$  should be measured.

32. The apparatus employed by Dulong and Petit for carrying out this method is represented in Fig. 31. The two upright tubes

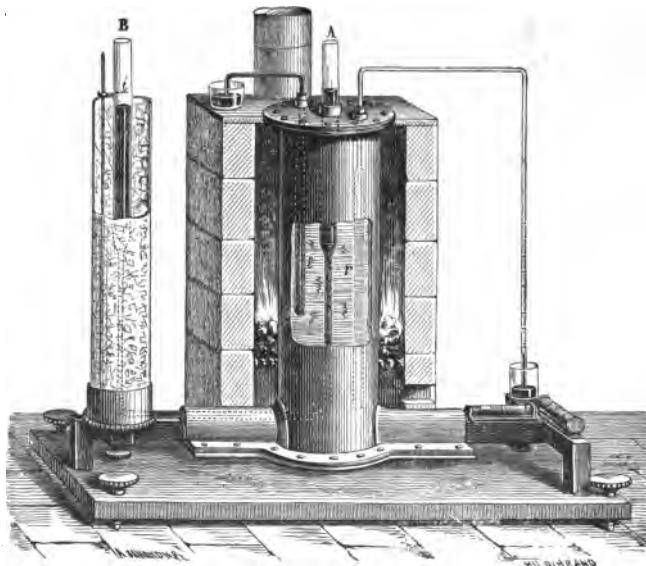


Fig. 31.—Apparatus of Dulong and Petit.

A, B, and the connecting tube at their base, rest upon a massive support furnished with levelling screws, and with two spirit-levels at right angles to each other, for insuring horizontality. The tube B is surrounded by a cylinder containing melted ice. The other tube A is surrounded by a copper cylinder filled with oil, which is heated by a furnace connected with the apparatus. In making an observation, the first step is to arrange the apparatus so that, when

the oil is heated to the temperature required, the mercury in the tube A may just be seen above the top of the cylinder, so as to be sighted with the telescope of a cathetometer; this may be effected by adding or taking away a small quantity of mercury. The extremity of the column B is next sighted, which gives the difference of the heights  $h'$  and  $h$ . The absolute height  $h$  is determined by means of a fixed reference mark  $i$  near the top of the column of mercury in the tube B. This reference mark is carried by an iron rod surrounded by the ice, and its distance from the axis of the horizontal connecting tube has been very accurately measured once for all. The temperature of the oil is given by the weight thermometer  $t$ , and by the air thermometer  $r$ , which latter we shall explain hereafter.

By means of this method Dulong and Petit ascertained that the expansion of mercury is nearly uniform between  $0^\circ$  and  $100^\circ$  C., as compared with the indications of an air-thermometer, and that though its expansion at higher temperatures is more rapid, the difference is less marked than in the case of other liquids. They found the mean coefficient of expansion from  $0^\circ$  to  $100^\circ$  to be  $\frac{1}{5550}$ ; from  $0^\circ$  to  $200^\circ$ ,  $\frac{1}{5425}$ ; and from  $0^\circ$  to  $300^\circ$ ,  $\frac{1}{5300}$ .

Regnault, without altering the principle of the apparatus of Dulong and Petit, introduced several improvements in detail, and added greatly to the length of the tubes A and B, thereby rendering the apparatus more sensitive. His results are not very different from those of Dulong and Petit. For example, he makes the mean coefficient from  $0^\circ$  to  $100^\circ$  to be  $\frac{1}{5509}$ ; from  $0^\circ$  to  $200^\circ$ ,  $\frac{1}{5479}$ ; and from  $0^\circ$  to  $300^\circ$ ,  $\frac{1}{5380}$ . His experiments show that the mean coefficient from  $0^\circ$  to  $50^\circ$  is  $\frac{1}{5547}$ , a value almost identical with  $\frac{1}{5550}$ .

**33. Expansion of Glass.**—The expansion of mercury being known, we can find the expansion of any kind of glass by observing the apparent expansion of mercury in a weight thermometer (§ 25) constructed of this glass, and subtracting this apparent expansion from the real expansion of the liquid; or more rigorously, by dividing the factor of real expansion of the liquid by the factor of apparent expansion (§ 20), we shall obtain the factor of expansion of the glass.

Dulong and Petit found  $\frac{1}{6480}$  as the mean value of the coefficient

of apparent expansion of mercury in glass, and  $\frac{1}{5550}$  as the coefficient of real expansion of mercury. The difference of these two fractions is approximately  $\frac{1}{38700}$ , which may therefore be taken as the coefficient of expansion of glass. It is about one-seventh of the coefficient of expansion of mercury.

**34. Expansion of any Liquid.**—The expansion of the glass of which a thermometer is made being known, we may use the instrument to measure the expansion of any liquid. For this purpose we must measure the capacity of the bulb and find how many divisions

of the stem it is equal to. We can thus determine how many divisions the liquid occupies at two different temperatures, that is, we can determine the apparent expansion of the liquid; and by adding to this the expansion of the glass, we shall obtain the real expansion of the liquid. Or more rigorously, we shall obtain the factor of real expansion of the liquid by multiplying together the factor of apparent expansion and the factor of expansion of the glass.

M. Pierre has performed an extensive series of experiments by this method upon a great number of liquids. The apparatus employed by him is shown in Fig. 32. The thermometer containing the given liquid is fixed beside a mercurial thermometer, which marks the temperature. The reservoir and a small part of the



Fig. 32.—Pierre's Apparatus.

tube are immersed in the bath contained in the cylinder below. The upper parts of the stems are inclosed in a second and smaller cylinder, the water in which is maintained at a sensibly constant temperature indicated by a very delicate thermometer.

From these experiments it appears that the expansions of liquids are in general much greater than those of solids; also that their ex-

pansion does not proceed uniformly, as compared with the indications of a mercurial thermometer, but increases very perceptibly as the temperature rises. This is shown by the following table:—

	Volume at 0°.	Volume at 10°.	Volume at 40°.
Water.....	1	1·000146	1·007492
Alcohol .....	1	1·010661	1·044882
Ether .....	1	1·015408	1·066863
Bisulphide of carbon...	1	1·011554	1·049006
Wood-spirit.....	1	1·012020	1·050509

**35. Other Methods.**—Another method of determining the apparent expansion of a liquid, with a view to deducing its real expansion, consists in weighing a glass bottle full of the liquid at different temperatures. This is virtually employing a weight thermometer.

A third method consists in observing the loss of weight of a piece of glass when weighed in the liquid at different temperatures. Time must be given in each case for the glass to take the temperature of the liquid; and when this condition is fulfilled, the factor of expansion will be equal to the loss of weight at the lower temperature, divided by the loss of weight at the higher.

For if the volume of the glass at the lower temperature be called unity, and its volume at the higher temperature  $1+g$ , the mass of liquid displaced at the lower temperature will be equal to its density  $d$ , and the mass displaced at the higher temperature will be the product of  $1+g$  by the density  $\frac{d}{1+l}$  where  $l$  denotes the expansion of the liquid. The losses of weight, expressed in gravitation measure, are therefore

$$d \text{ and } \frac{(1+g) d}{1+l},$$

and the former of these divided by the latter gives  $\frac{1+l}{1+g}$ , which (§ 20) is the factor of apparent expansion.

**36. Formulae for the Expansion of Liquids.**—As we have mentioned above, the expansion of liquids does not advance uniformly with the temperature; whence it follows that the mean coefficient of expansion will vary according to the limiting temperatures between which it is taken.

For a great number of liquids, the mean coefficient of expansion may be taken as increasing uniformly with the temperature. If, therefore,  $\Delta$  be the expansion from 0 to  $t$ , we have

$$\frac{\Delta}{t} = a + bt, \text{ whence } \Delta = at + bt^2,$$

*a* and *b* being two constants specifying the expansibility of the given liquid.

For some very expansible liquids two constants are not sufficient, and the expansion is represented by the formula

$$\Delta = at + bt^2 + ct^3.$$

We subjoin a few instances of this class taken from the work of M. Pierre:—

Alcohol..... $\Delta = 0\cdot0010486 t + 0\cdot0000017510 t^2 + 0\cdot00000000134518 t^3$

Ether..... $\Delta = 0\cdot0015182 t + 0\cdot0000023592 t^2 + 0\cdot000000040051 t^3$

Bisulphide of carbon.... $\Delta = 0\cdot0011398 t + 0\cdot0000018707 t^2 + 0\cdot00000019123 t^3$

Bromine..... $\Delta = 0\cdot0010382 t + 0\cdot0000017114 t^2 + 0\cdot0000000054471 t^3$

**37. Maximum Density of Water.**—Water, unlike other liquids, contracts as its temperature rises from  $0^\circ$  to  $4^\circ$ , at which point its volume is a minimum, and therefore its density a maximum.

The following experiment, which furnishes a means of determining the temperature of maximum density, is due to Hope.

A glass jar is employed, having two lateral openings, one near the top and the other near the bottom, which admit two thermometers placed horizontally. The jar is filled with water at a temperature higher than  $4^\circ$ , and its middle is surrounded with a freezing-mixture. The following phenomena will then be observed.

The lower thermometer descends steadily to  $4^\circ$ , and there remains stationary. The upper thermometer at first undergoes very little change, but when the lower one has reached the fixed temperature, the upper one begins to fall, reaches the temperature of zero, and,

finally, the water at the surface freezes, if the action of the freezing-mixture continues for a sufficiently long time. These facts admit of a very simple explanation.

As the water in the middle portion of the jar grows colder, its density increases, and it sinks to the bottom. This process goes on till all the water in the lower part has attained the temperature of  $4^\circ$ . But when all the water from the centre to the bottom has attained this temperature, any further cooling of the water in the centre will produce no circulation in the lower portion, and

very little in the upper, until needles of ice are formed. These, being lighter than water, rise to the surface, and thus produce a circulation

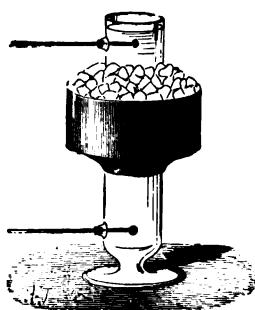


Fig. 38.  
Hope's Experiment.

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MAXIMUM DENSITY OF WATER.

37

which causes the water near the surface to freeze, while that near the bottom remains at the temperature of  $4^{\circ}$ .

This experiment illustrates what takes place during winter in pools of fresh water. The fall of temperature at the surface does not extend to the bottom of the pool, where the water, whatever be the external temperature, seldom falls below  $4^{\circ}$ . This is a fact of great interest, as exemplifying the close connection of natural phenomena, and the manner in which they contribute to a common end. It is in virtue of this anomaly exhibited by water in its expansion, taken in conjunction with the specific lightness of ice and the low conducting power of liquids generally, that the temperature at the bottom of deep pools remains moderate even during the severest cold, and that the lives of aquatic animals are preserved.

**38. Saline Solutions.**—These remarks are not applicable to sea-water, which contracts as its temperature falls till its freezing-point is attained; this latter being considerably lower than the freezing-point of fresh water.

In the case of saline solutions of different strengths, the temperature of maximum density falls along with the freezing-point, and falls more rapidly than this latter, so that for solutions containing more than a certain proportion of salt the temperature of maximum density is below the freezing-point. In order to show this experimentally, the solution must be placed in such circumstances as to remain liquid at a temperature below its ordinary freezing-point.

**39. Apparent Expansion of Water.**—Fig. 34 represents an apparatus for showing the changes of apparent volume of water in a glass vessel. In the centre are two thermometers, one containing alcohol and the other water. The reservoir of the latter is a long spiral, surrounding the reservoir of the alcohol thermometer and having much greater capacity. Both reservoirs are contained in a metal box, which is at first filled with melting ice. The two instruments are so placed that at zero the extremities of the two liquid columns are on the same horizontal line. This being the case, if the

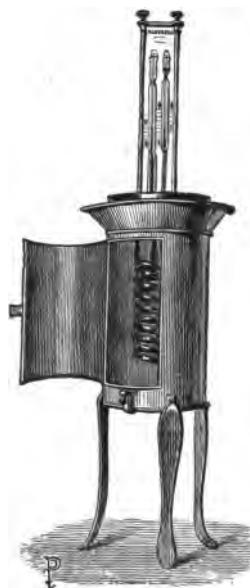


Fig. 34.  
Maximum Density of Water.

ice be now removed, and the apparatus left to itself, or if the process be accelerated by placing a spirit-lamp below the box, the alcohol will immediately be seen to rise, while the water will descend; and the two liquids will thus continue to move in opposite directions until a temperature of  $5^{\circ}$  or  $6^{\circ}$  is attained. From this moment the water ceases to descend, and begins to move in the same direction as the alcohol. The temperature at which the water thermometer becomes stationary is that at which the coefficient of expansion of water is the same as that of glass. The coefficient of expansion of water is zero at  $4^{\circ}$ , and at temperatures near  $4^{\circ}$  is approximately

$$.000016 (t - 4).$$

The average value of the coefficient of expansion of glass is about .000027, and by equating these two expressions, we have

$$t - 4 = \frac{27}{16} = 1.7 \text{ nearly};$$

hence the water thermometer will be stationary at the temperature  $5^{\circ}.7$ .

**40. Density of Water at Various Temperatures.**—The volume, at temperatures near  $4^{\circ}$ , of a quantity of water which would occupy unit volume at  $4^{\circ}$ , is approximately

$$1 + .000008 (t - 4)^2,$$

and the density of water at these temperatures is therefore

$$1 - .000008 (t - 4)^2,$$

the density at  $4^{\circ}$  being taken as unity.

The density of water at some other temperatures is given in the following table:—

Temperature.	Density.
$0^{\circ}$ .....	.999871
$4^{\circ}$ .....	1.000000
$8^{\circ}$ .....	.999886
$12^{\circ}$ .....	.999549
$16^{\circ}$ .....	.999002
$20^{\circ}$ .....	.998259
$50^{\circ}$ .....	.9882
$100^{\circ}$ .....	.9586

**41. Expansion of Iron and Platinum.**—The coefficient of absolute



Fig. 35.—Expansion of Iron and Platinum.

expansion of mercury being known, that of glass is deduced from it in the manner already indicated (§ 33). Du-

long and Petit have deduced from it also the coefficients of expan-

sion of iron and platinum, these metals not being attacked by mercury. The method employed is the following.

The metal in question is introduced, in the shape of a cylindrical bar, into the reservoir of a weight thermometer. Let  $W$  be the weight of the metal introduced, and  $D$  its density at zero. The process is the same as in using the weight thermometer; that is, after having filled the reservoir with mercury at  $0^\circ \text{ C.}$ , we observe the weight  $w$  of the metal which issues at a given temperature  $t$ . The volume at  $0^\circ \text{ C.}$  of the mercury which has issued, is  $\frac{w}{d}$ ,  $d$  being the density of mercury at zero; the volume at  $t^\circ$  is therefore  $\frac{w}{d}(1+mt)$ ,  $m$  being the coefficient of expansion of mercury. This volume evidently represents the expansion of the metal, *plus* that of the mercury, *minus* that of the glass. If then  $M$  denote the weight of mercury that fills the apparatus at  $0^\circ \text{ C.}$ , and if  $K$  be the coefficient of cubical expansion of glass, and  $x$  the expansion of unit volume of the given metal, we have the equation

$$\frac{w}{d}(1+mt) = \frac{W}{D}x + \frac{M}{d}mt - \left(\frac{W}{D} + \frac{M}{d}\right)Kt,$$

whence we can find  $x$ .

**42. Convection of Heat in Liquids.**—When different parts of a liquid or gas are heated to different temperatures, corresponding differences of density arise, leading usually to the formation of currents. This phenomenon is called *convection*.

Thus, for instance, if we apply heat to the bottom of a vessel containing water, the parts immediately subjected to the action of the heat expand and rise to the surface; they are replaced by colder portions, which in their turn are heated and ascend; and thus a continual circulation is maintained. The ascending and descending currents can be rendered visible by putting oak sawdust into the water.

**43. Heating of Buildings by Hot Water.**—This is a simple application of the principle just stated. One of the most common arrangements for this purpose is shown in Fig. 36. The boiler  $C$  is heated by a fire below it, and the products of combustion escape through the chimney  $A B$ . At the top of the house is a reservoir  $D$ , communicating with the boiler by a tube. From this reservoir the liquid flows into another reservoir  $E$  in the story immediately below, thence into another reservoir  $F$ , and so on. Finally, the last of these

reservoirs communicates with the bottom of the boiler. The boiler, tubes, and reservoirs are all completely filled with water, with the

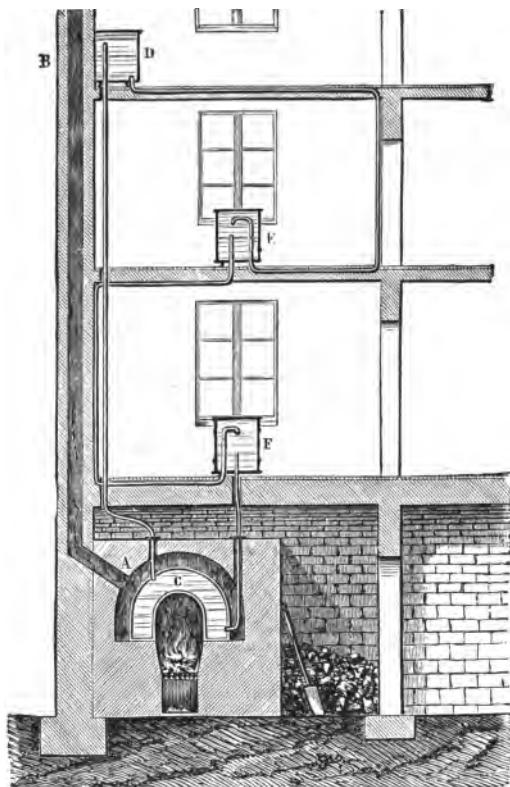


Fig. 36.—Heating by Hot Water.

exception of a small space left above in order to give room for the expansion of the liquid. An ascending current flows through the left-hand tube, and the circulation continues with great regularity, so long as the temperature of the water in the boiler remains constant.

## CHAPTER V.

### EXPANSION OF GASES.

44. **Experiments of Gay-Lussac.**—Gay-Lussac conducted a series of researches on the expansion of gases, the results of which were long regarded as classical. He employed a thermometer with a large reservoir A, containing the gas to be operated on; an index of mercury *m* separated the gas from the external air, while leaving it full liberty to expand. The gas had previously been dried by pass-

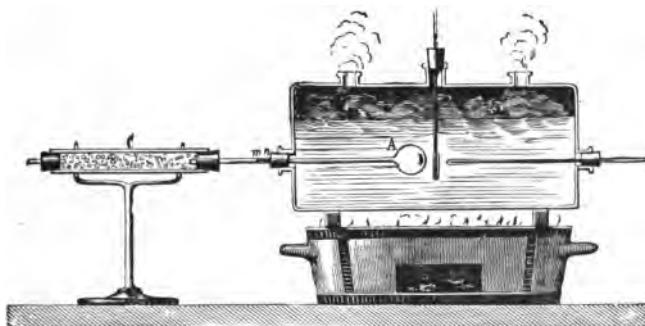


Fig. 87.—Gay-Lussac's Apparatus.

ing it through a tube containing chloride of calcium, or some other desiccating substance. The thermometer was first placed in a vessel filled with melting ice, and when the gas had thus been brought to  $0^{\circ}$  C., the tube was so adjusted that the index coincided with the opening through which the thermometer passed.

The tube and reservoir having been previously gauged, and the former divided into parts of equal capacity, the apparent volume of the gas (expressed in terms of these divisions) is indicated by the position of the index; let the apparent volume observed at  $0^{\circ}$  C. be called *n*, and let *H* denote the external pressure as indicated by a

barometer. The apparatus is then raised to a known temperature  $t$  by means of the furnace below the vessel, and the stem of the thermometer is moved until the index reaches the edge of the opening. Let  $n'$  be the apparent volume of the gas at this new temperature, and as the external pressure may have varied, let it be denoted by  $H'$ . The real volumes of the gas will be as  $n$  to  $n' (1+gt)$ , where  $g$  denotes the mean coefficient of expansion of the glass; and the products of volume and pressure will be as  $n H$  to  $n' (1+gt) H'$ . Hence if  $\alpha$  denote the mean coefficient of expansion of the air, we have

$$n H (1 + \alpha t) = n' (1 + gt) H';$$

from which equation  $\alpha$  can be determined.

By means of this method Gay-Lussac verified the law previously announced by Sir Humphry Davy for air, that the coefficient of expansion is independent of the pressure. He also arrived at the result that this coefficient is sensibly the same for all gases. He found its value for dry air to be .00375. This result, which was for a long time the accepted value, is now known to be in excess of the truth. Rudberg, a Swedish philosopher, was the first to point out the necessity for using greater precautions to insure the absence of moisture, which adheres to the glass with great tenacity at the lower temperature, and, by going off into vapour when heated, adds to the volume of the air at the higher temperature. He found that the last traces of vapour could only be removed by repeatedly exhausting the vessel with an air-pump when heated, and refilling it with dried air. Another weak point in the method employed by Gay-Lussac was the shortness of the mercurial index, which, in conjunction with the fact that mercury does not come into close contact with glass (as proved by the fact of its not wetting it), allowed a little leakage in both directions. These imperfections have been remedied in later investigations, of which the most elaborate are those of Regnault. He employed four distinct methods, of which we shall only describe one.

**45. Regnault's Apparatus.**—The glass vessel BC (Fig. 38) containing the air to be experimented on, is connected with the T-shaped piece EI, the branch I of which communicates, through desiccating tubes, with an air-pump, and is hermetically closed with a blow-pipe after the vessel has received its charge of dry air; while the branch ED communicates with the top of a mercurial manometer. A mark is made at a point  $b$  in the capillary portion of the tube, and in every

observation the mercury in the manometer is made to reach exactly to this point, either by pouring in more mercury at the top M' of the other tube of the manometer, or by allowing some of the liquid to escape through the cock R at the bottom. The air under experiment is thus always observed at the same apparent volume, and the observation gives its pressure. The vessel B is inclosed within a



Fig. 38.—Regnault's Apparatus.

boiler, which consists of an inner and an outer shell, with a space between them, through which the steam circulates when the water boils.

In reducing the observations, the portion of the glass vessel within the boiler is regarded as having the temperature of the water in the boiler, while the portion of the tube external to the boiler is regarded as having the temperature of the surrounding air.

In this mode of operating, the volume, or at least the apparent volume, is constant, so that the coefficient  $a$  which is determined is substantially defined by the equation

$$P_t = P_0 (1 + at),$$

$P_0$  and  $P_1$  denoting the pressures at constant volume. The coefficient thus defined should be called the *coefficient of increase of pressure*. It is often called the "coefficient of expansion at constant volume," which is a contradiction in terms.

In another mode of operating Regnault observed the expansion at constant pressure, and thus determined the *coefficient of expansion* properly so called. A small but steady difference was found between the two. If Boyle's law were exact they would be identical. As a matter of fact, the coefficient of increase of pressure was found, in the case of air and all gases except hydrogen, to be rather less than the coefficient of expansion. In other words, the product of volume and pressure at one and the same temperature  $t^\circ$  was found to be least when the volume was least; a result which accords with Regnault's direct observations on Boyle's law.

**46. Results.**—The following table contains the final results for the various gases which were submitted to experiment:—

	Coefficient of increase of pressure at con- stant volume.	Coefficient of increase of volume at con- stant pressure.
Air.....	0·003665	..... 0·003670
Nitrogen.....	0·003668	.....
Hydrogen.....	0·003667	..... 0·003661
Carbonic oxide .....	0·003667	..... 0·003669
Carbonic acid .....	0·003688	..... 0·003710
Nitrous oxide.....	0·003676	..... 0·003720
Cyanogen.....	0·003829	..... 0·003877
Sulphurous acid .....	0·003845	..... 0·003903

It will be observed that the largest values of the coefficients belong to those gases which are most easily liquefied.

We may add that the coefficients increase very sensibly with the pressure; thus between the pressures of one and of three atmospheres the coefficient of expansion of air increases from '00367 to '00369. This increase is still more marked in the case of the more liquefiable gases.

**47. Reduction to the Fahrenheit Scale.**—The coefficient of expansion of any substance per degree Fahrenheit is  $\frac{1}{2}$  of the coefficient per degree Centigrade; the volume at  $32^\circ$  F. being made the standard from which expansions are reckoned, so that if  $V_0$  denote the volume at this temperature and  $V$  the volume at  $t^\circ$  F., the coefficient of expansion  $\alpha$  is defined by the equation

$$V = V_0 \{1 + \alpha (t - 32)\}.$$

**48. Air-thermometer.**—The close agreement between the expansions of different gases, and between the expansions of the same gas at different pressures, is a strong reason for adopting one of these bodies as the standard substance for the measurement of temperature by expansion, rather than any particular liquid.

Moreover, the expansion of gases being nearly twenty times as great as that of mercury, the expansion of the containing vessel will be less important; the apparent expansion will be nearly the same as the real expansion, and differences of quality in the glass will not sensibly affect the comparability of different thermometers.

Air-thermometers have accordingly been often used in delicate investigations. They consist, like other thermometers, of a reservoir and tube; but the latter, instead of being sealed, is left open. This open end, in one form of the instrument, is pointed downwards, and immersed in a liquid; usually mercury, which rises to a greater or less distance up the tube as the air in the thermometer contracts or expands. As variations of pressure in the surrounding air will also affect the height of this column of liquid, it is necessary to take readings of the barometer, and to make use of them in reducing the indications of the air-thermometer. Even if the barometer continues steady, it is still necessary to apply a correction for changes of pressure; since the difference between the pressure in the air-thermometer and that of the external air is not constant, but is proportional to the height of the column of liquid.

In the form of air-thermometer finally adopted by Regnault, the air in the instrument was kept at constant (apparent) volume, and its variations of pressure were measured, the apparatus employed being precisely that which we have described in § 45.

**49. Perfect Gas.**—In discussions relating to the molecular constitution of gases, the name *perfect gas* is used to denote a gas which would exactly fulfil Boyle's law; and molecular theories lead to the conclusion that for all such gases the coefficients of expansion would be equal. Actual gases depart further from these conditions as they are more compressed below the volumes which they occupy at atmospheric pressure; and it is probable that when very highly rarefied they approach the state of "perfect gases" very closely indeed.

**50. Absolute Temperature by Air-thermometer.**—*Absolute temperature by the air-thermometer* is usually defined by the condition that the temperature of a given mass of air at constant pressure is to be regarded as *proportional to its volume*. If the difference of

temperature between the two ordinary fixed points be divided into a hundred degrees, as in the ordinary Centigrade thermometer, the two fixed points themselves will be called respectively  $273^{\circ}$  and  $373^{\circ}$ ; since air expands by  $\frac{1}{273}$  of its volume at the lower fixed point for each degree, and therefore by  $\frac{100}{273}$  of this volume for a hundred degrees.

There is some advantage in altering the definition so as to make the temperature of a given mass of air at constant volume *proportional to its pressure*. The two fixed points will then be  $273^{\circ}$  and  $373^{\circ}$  as above, and the zero of the scale will be that temperature at which the pressure vanishes.

The advantage of the second form of definition is that it enables us to continue our scale down to this point—called absolute zero—without encountering any physical impossibility, such as the conception of reducing a finite quantity of air to a mathematical point, which would be required according to the first form of definition.

Practically, “absolute temperatures by air-thermometer” are computed by adding 273 to ordinary “temperatures by air-thermometer,” these latter being expressed on the Centigrade scale. We shall employ the capital letter T to denote absolute temperature, and the small letter t to denote ordinary temperature. We have

$$T = 273 + t,$$

and the general law connecting the volume, pressure, and temperature of a gas is

$$\frac{VP}{T} = \text{constant};$$

or, introducing the density D instead of the volume V,

$$\frac{P}{DT} = \text{constant}.$$

As above explained, these laws, though closely approximate in ordinary cases, are not absolutely exact.

**51. Pyrometers.**—The measurement of high temperatures such as those of furnaces is very difficult. Instruments for this purpose are called pyrometers. One of the best is the air-thermometer employed by Deville and Troost, having a bulb of hard porcelain.

**52. Density of Gases.**—The *absolute density* of a gas—that is, its mass per unit volume—which is denoted by D in the above formula, is proportional, as the formula shows, to  $\frac{P}{T}$ , and may therefore

undergo enormous variation. In stating the *relative density* of a gas as compared with air, the air and the gas are supposed to be at the same pressure and temperature. For purposes of great accuracy this pressure and temperature must be specified, since, as we have seen, there are slight differences in the changes produced in different gases by the same changes of pressure and temperature. The comparison is generally supposed to be made at the temperature  $0^{\circ}$  C., and at the pressure of one standard atmosphere.

**53. Measurement of the Relative Density of a Gas.**—The densities of gases have been the subject of numerous investigations; we shall describe only the method employed by Regnault.

The gas is inclosed in a globe, of about 12 litres capacity (Fig. 39), furnished with a stop-cock leading to a three-way tube, one of whose branches is in communication with a manometer, and the other with an air-pump. The globe is exhausted several times, and each time the gas is dried on its way to the globe by passing through a number of tubes containing pieces of pumice-stone moistened with sulphuric acid. When all moisture has been removed, the globe is surrounded with melting ice, and is kept full of gas at the pressure of the atmosphere till sufficient time has been given for its contents to assume the temperature of the melting ice. The stop-cock is then closed, the globe is taken out, carefully dried, and allowed to take the temperature of the atmosphere. It is then weighed with a delicate balance.

The experiment is repeated, with no change except that by means of the air-pump the gas in the globe is reduced to as small a pressure as possible. Let this pressure be denoted by  $h$ , and the atmospheric pressure in the previous experiment by  $H$ . Then the difference of the two weights is the weight of as much gas at temperature  $0^{\circ}$  and pressure  $H - h$  as would fill the globe. Let  $w$  denote this difference, and let  $w'$  be the difference between two weighings made in the same

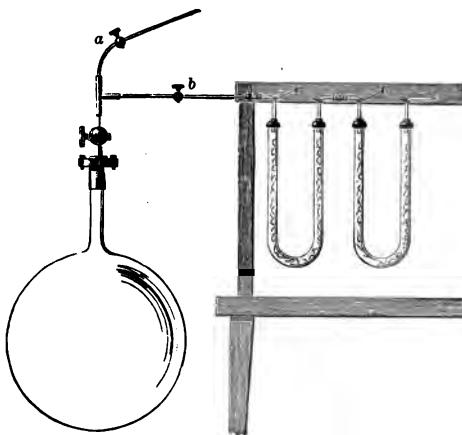


Fig. 39.—Measurement of Density of Gases.

manner with dry air in the globe at pressures  $H'$  and  $h'$ . Then the relative density of the gas will be

$$\frac{w}{w'} \frac{H' - h'}{H - h'}$$

We must now describe a special precaution which was employed by Regnault (and still earlier by Dr. Prout) to avoid errors in weighing arising from the varying weight of the external air displaced by the globe.

A second globe (Fig. 40) of precisely the same external volume as the first, made of the same glass, and closed air-tight, was used as a counterpoise. The equality of external volumes was ensured in the following way.

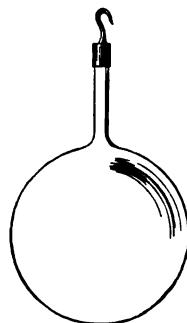


Fig. 40.  
Compensating Globe.

The globes were filled with water, hung from the two scales of a balance, and equilibrium was brought about by putting a sufficient quantity of some material into one scale. Both globes, thus hanging from the scales in equilibrium, were then immersed in water, and if this operation disturbed the equilibrium it was known that the external volumes were not equal. Let  $p$  be the weight which must be put into one scale to restore equilibrium; then this weight of water represents the difference of the two external volumes; and the next operation was to prepare a small piece of glass tube closed at the ends which should lose  $p$  when weighed in water. The larger of the two globes was used for containing the gases to be weighed, and the smaller globe along with this piece of tube constituted the counterpoise. Since the volume of the gas globe was exactly the same as that of the counterpoise, the pressure of the external air had no tendency to make either preponderate, and variations in the condition of this air, whether as regards pressure, temperature, or humidity, had no disturbing effect.

**54. Absolute Densities.**—In order to convert the preceding relative determinations into absolute determinations, it is only necessary to know the precise internal volume of the globe at the temperature  $0^{\circ} \text{ C}$ . In order to determine this with the utmost possible exactness the following operations were performed.

The globe was first weighed in air, with its stop-cock open, the temperature of the air and the height of the barometer being noted.

It was then filled with water, special precautions being taken to expel every particle of air; and was placed for several hours in the midst of melting ice, to insure its being filled with water at 0° C.

The stop-cock was then closed, and the globe was left for two hours in a room which had a very steady temperature of 6°. It was then weighed in this room, the height of the barometer being at the same time observed. The difference between this weight and that of the globe before the introduction of the water, was the weight of the water *minus* the weight of the same volume of air, subject to a small correction for change of density in the external air between the two weighings, which, with the actual heights of the barometer and thermometer, was insensible.

The weight of water at 0° which the globe would hold at 0° was therefore known; and hence the weight of water at 4° (the temperature of maximum density) which the globe would hold at 0° was calculated, from the known expansion of water. This weight, in grammes, is equal to the capacity in cubic centimetres.

The result thus obtained was that the capacity of the globe at 0° was 9881 cubic centimetres; and the weight of the dry air which filled it at 0° and a pressure of 760<sup>mm</sup> was 12·778 grammes. Hence the weight (or mass) of 1 cubic centimetre of such air is .0012932 gramme.

This experiment was performed at Paris, where the value of *g* (the intensity of gravity) is 980·94; and since the density of mercury at 0° is 13·596, the pressure of 76 centimetres of mercury was equivalent to

$$76 \times 13\cdot596 \times 980\cdot94 = 1\cdot0136 \times 10^6$$

dynes per square centimetre.

If we divide the density just found by 1·0136, we obtain the density of air at 0° and a pressure of a million dynes per square centimetre, which is a convenient standard for general reference; we have thus

$$.0012932 \div 1\cdot0136 = .0012759.$$

A litre or cubic decimetre contains 1000 cubic centims. Hence the weight of a litre of air in the standard condition adopted by Regnault is 1·2932 gramme.

The following table gives the densities of several gases at 0° C. at a pressure of 760 millimetres of mercury at Paris.

Name of Gas.	Relative Density.	Mass of a Litre in Grammes.
Air.....	1	1.2932
Oxygen.....	1.10563	1.4298
Hydrogen .....	.08926	.08957
Nitrogen.....	.97137	1.25615
Chlorine.....	2.4216	3.1328
Carbonic oxide.....	.9569	1.2344
Carbonic acid.....	1.52901	1.9774
Protoxide of nitrogen.....	1.5289	1.9697
Binoxide of nitrogen.....	1.0388	1.3434
Sulphurous acid.....	2.1930	2.7289
Cyanogen.....	1.8064	2.3302
Marsh-gas .....	.559	.727
Olefiant gas.....	.985	1.274
Ammonia.....	.5967	7697

55. **Draught of Chimneys.**—The expansion of air by heat produces the upward current in chimneys, and an approximate expression for the velocity of this current may be obtained by the application of Torricelli's theorem on the efflux of fluids from orifices (see Part I.).

Suppose the chimney to be cylindrical and of height  $h$ . Let the air within it be at the uniform temperature  $t'$  Centigrade, and the external air at the uniform temperature  $t$ . According to Torricelli's theorem, the square of the linear velocity of efflux is equal to the product of  $2g$  into the head of fluid, the term *head of fluid* being employed to denote the *pressure* producing efflux, *expressed in terms of depth of the fluid*.

In the present case this head is the difference between  $h$ , which is the height of air within the chimney, and the height which a column of the external air of original height  $h$  would have if expanded upwards, by raising its temperature from  $t$  to  $t'$ . This latter height is  $h \frac{1+at'}{1+at}$ ;  $a$  denoting the coefficient of expansion .00366; and the head is

$$h \frac{1+at'}{1+at} - h = \frac{ha(t' - t)}{1+at}.$$

Hence, denoting by  $v$  the velocity of the current up the chimney, we have

$$v^2 = \frac{2gha(t' - t)}{1+at}.$$

This investigation, though it gives a result in excess of the truth, from neglecting to take account of friction and eddies, is sufficient to explain the principal circumstances on which the strength of draught

depends. It shows that the draught increases with the height  $h$  of the chimney, and also with the difference  $t' - t$  between the internal and external temperatures.

The draught is not so good when a fire is first lighted as after it has been burning for some time, because a cold chimney chills the



Fig. 41.—Rumford's Fireplace.

air within it. On the other hand, if the fire is so regulated as to keep the room at the same temperature in all weathers, the draught will be strongest when the weather is coldest.

The opening at the lower end of the chimney should not be too wide nor too high above the fire, as the air from the room would then enter it in large quantity, without being first warmed by passing through the fire. These defects prevailed to a great extent in old chimneys. Rumford was the first to attempt rational improvements. He reduced the opening of the chimney and the depth of the fireplace, and added polished plates inclined at an angle, which serve both to guide the air to the fire and to reflect heat into the room (Fig. 41).

The blower (Fig. 42) produces its well-known effects by compelling all air to pass through the fire before entering the chimney. This at once improves the draught of the chimney by raising the

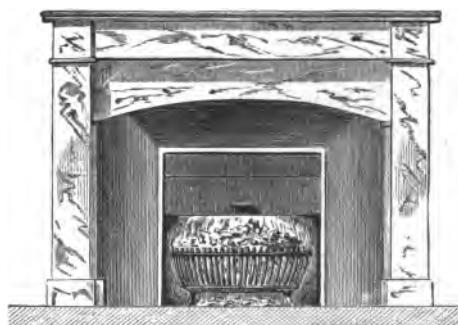


Fig. 42.—Fireplace with Blower.

temperature of the air within it, and quickens combustion by increasing the supply of oxygen to the fuel.

**56. Stoves.**—The heating of rooms by open fireplaces is effected almost entirely by radiation, and much even of the radiant heat is wasted. This mode of heating then, though agreeable and healthful, is far from economical. Stoves have a great advantage in point of economy; for the heat absorbed by their sides is in great measure given out to the room, whereas in an ordinary fireplace the greater part of this heat is lost. Open fireplaces have, however, the advantage as regards ventilation; the large opening at the foot of the chimney, to which the air of the room has free access, causes a large body of air from the room to ascend the chimney, its place being supplied by fresh air entering through the chinks of the doors and windows, or any other openings which may exist.

Stoves are also liable to the objection of making the air of the room too dry, not, of course, by removing water, but by raising the temperature of the air too much above the dew-point (Chap. xi.). The same thing occurs with open fireplaces in frosty weather, at which time the dew-point is unusually low. This evil can be remedied by placing a vessel of water on the stove. The reason why it is more liable to occur with stoves than with open fireplaces, is mainly that the former raise the air in the room to a higher temperature than the latter, the defect of air-temperature being in the latter case compensated by the intensity of the direct radiation from the glowing fuel.

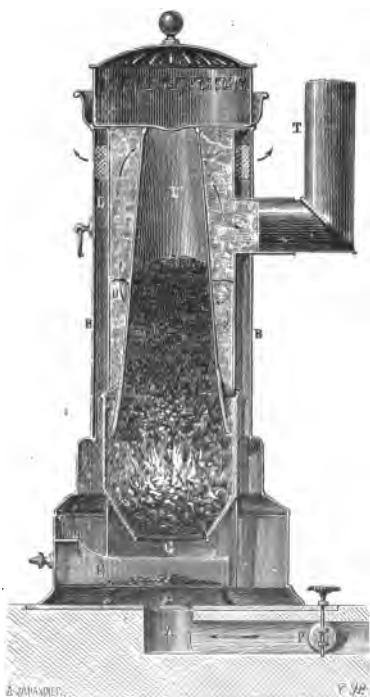


Fig. 43.—Ventilating Stove.

situation it prevents the wasteful escape of heat backwards into the chimney, and keeps the back of the fire nearly as hot as the centre.

As a lining to stoves, it impedes the lateral escape of heat, thus answering the double purpose of preventing the sides of the stove from overheating, and at the same time of keeping up the temperature of the fire, and thereby promoting complete combustion. Its use must, however, be confined to that portion of the stove which serves as the fire-box, as it would otherwise prevent the heat from being given out to the apartment.

The stove represented in Fig. 43 belongs to the class of what are called in France *calorifères*, and in England *ventilating stoves*, being constructed with a view to promoting the circulation and renewal of the air of the apartment. G is the fire-box, over which is the feeder U, containing unburned fuel, and tightly closed at top by a lid, which is removed only when fresh fuel is to be introduced. The ash-pan F has a door pierced with holes for admitting air to support combustion. The flame and smoke issue at the edge of the fire-box, and after circulating round the chamber O which surrounds the feeder, enter the pipe T which leads to the chimney. The chamber O is surrounded by another inclosure L, through which fresh air passes, entering below at A, and escaping into the room through perforations in the upper part of the stove as indicated by the arrows. The amount of fresh air thus admitted can be regulated by the throttle-valve P.

## CHAPTER VI.

### CALORIMETRY.

**57. Quantity of Heat.**—We have discussed in previous chapters the measurement of temperature, and have seen that it is to a great extent arbitrary, since intervals of temperature which are equal as measured by the expansion of one substance are not equal as measured by the expansion of another.

The measurement of quantities of heat stands upon an entirely different footing. There is nothing arbitrary or conventional in asserting the equality or inequality of two quantities of heat.

**58. Principles Assumed.**—The two following principles may be regarded as axiomatic.

(1) The heat which must be given to a body to raise it through a given range of temperature at constant pressure, is equal to that which the body gives out in falling through the same range of temperature under the same pressure. For instance, the heat which must be given to a gramme of water, to raise its temperature from  $5^{\circ}$  to  $10^{\circ}$ , is equal to that which is given out from the same water when it falls from  $10^{\circ}$  to  $5^{\circ}$ .

(2) In a homogeneous substance equal portions require equal quantities of heat to raise them from the same initial to the same final temperature; so that, for example, the heat required to raise two grammes of water from  $5^{\circ}$  to  $10^{\circ}$  is double of that which is required to raise one gramme of water from  $5^{\circ}$  to  $10^{\circ}$ .

**59. Cautions.**—We are not entitled to assume that the quantities of heat required to raise a given body through equal intervals of temperature—for example, from  $5^{\circ}$  to  $10^{\circ}$ , and from  $95^{\circ}$  to  $100^{\circ}$ —are equal. Indeed we have already seen that the equality of two intervals of temperature is to a considerable extent a matter of mere

convention; temperature being conventionally measured by the expansion (real or apparent) of some selected substance.

It would, however, be quite possible to adopt a scale of temperature based on the elevation of temperature of some particular substance when supplied with heat. We might, for instance, define a degree (at least between the limits  $0^{\circ}$  and  $100^{\circ}$ ) as being the elevation of temperature produced in water of any temperature by giving it one hundredth part of the heat which would be required to raise it from  $0^{\circ}$  to  $100^{\circ}$ .

Experiments which will be described later show that if air or any of the more permanent gases were selected as the standard substance for thus defining equal intervals of temperature, the scale obtained would be sensibly the same as that of the air-thermometer; and the agreement is especially close when the gases are in a highly rarefied condition.

**60. Unit of Heat.**—We shall adopt as our unit, in stating quantities of heat, the heat required to raise a gramme of cold water through one degree Centigrade. This unit is called, for distinction, the gramme degree. The kilogramme-degree and the pound-degree are sometimes employed, and are in like manner defined with reference to cold water as the standard substance.

There is not at present any very precise convention as to the temperature at which the cold water is to be taken. If we say that it is to be within a few degrees of the freezing-point, the specification is sufficiently accurate for any thermal measurements yet made.

**61. Thermal Capacity.**—If a quantity  $Q$  of heat given to a body raises its temperature from  $t_1^{\circ}$  to  $t_2^{\circ}$ , the quotient

$$\frac{Q}{t_2 - t_1}$$

of the quantity of heat given by the rise of temperature which it produces, is called the *mean thermal capacity* of the body between the temperatures  $t_1^{\circ}$  and  $t_2^{\circ}$ .

As  $t_2$  is brought nearer to  $t_1$ , so as to diminish the denominator, the numerator  $Q$  will also diminish, and in general very nearly in the same proportion. The limit to which the fraction approaches as  $t_2$  is brought continually closer to  $t_1$  is called the *thermal capacity* of the body at the temperature  $t_1^{\circ}$ . That is, in the language of the differential calculus, the thermal capacity at  $t^{\circ}$  is  $\frac{dQ}{dt}$ .

From the way in which we have defined our unit of heat, it fol-

lows that the thermal capacity of any quantity of cold water is numerically equal to its mass expressed in grammes; and that the number which expresses the thermal capacity of any body may be regarded as expressing the quantity of water which would receive the same rise of temperature as the body from the addition of the same quantity of heat. This quantity of water is often called the *water-equivalent* of the body.

**62. Specific Thermal Capacities.**—The thermal capacity of unit mass of a substance is called the *specific heat* of the substance; and it is always to be understood that the same unit of mass is employed for the substance as for the water which is mentioned in the definition of the unit of heat. Specific heat is therefore independent of units, and merely expresses the ratio of the two quantities of heat which would raise equal masses of the given substance and of cold water through the same small difference of temperature. Or we may regard it as the ratio of two masses, the first, of cold water, and the second of the substance in question, which have the same thermal capacity.

There is another specific thermal capacity which it is often necessary to consider, namely, the *thermal capacity of unit volume* of a substance. It has not received any brief name. It is equal to the mass of unit volume multiplied by the thermal capacity of unit mass; in other words, it is equal to the *product of the density and the specific heat* of the substance.

It is evident, from what precedes, that the heat required to raise  $m$  grammes of a substance through  $t$  degrees is  $mst$ , where  $s$  denotes the mean specific heat between the initial and the final temperature; and the same expression denotes the quantity of heat which the body in question loses in cooling down through  $t$  degrees.

**63. Method of Mixtures.**—Let  $m_1$  grammes of a substance of specific heat  $s_1$  and temperature  $t_1^\circ$  be mixed with  $m_2$  grammes of a substance of specific heat  $s_2$  and temperature  $t_2^\circ$ , the mixture being merely mechanical, so that no heat is generated or absorbed by any action between the substances, and all external gain or loss of heat being prevented. Then the warmer substance will give heat to the colder, until they both come to a common temperature, which we will denote by  $t$ . The warmer substance, which we will suppose to be the former, will have cooled down through the range  $t_1 - t$ , and will have lost  $m_1 s_1 (t_1 - t)$  units of heat. The colder substance will have risen through the range  $t - t_2$ , and will have gained  $m_2 s_2 (t - t_2)$

units of heat. These two expressions represent the same thing, namely, the heat given by the warmer body to the colder. We may therefore write

$$m_1 s_1 (t_1 - t) = m_2 s_2 (t - t_2), \quad (1)$$

that is,

$$m_1 s_1 t_1 + m_2 s_2 t_2 = (m_1 s_1 + m_2 s_2) t, \quad (2)$$

whence

$$t = \frac{m_1 s_1 t_1 + m_2 s_2 t_2}{m_1 s_1 + m_2 s_2}. \quad (3)$$

If there are more than two components in the mixture, similar reasoning will still apply; thus, if there are three components, the resulting temperature will be

$$t = \frac{m_1 s_1 t_1 + m_2 s_2 t_2 + m_3 s_3 t_3}{m_1 s_1 + m_2 s_2 + m_3 s_3}. \quad (4)$$

Strictly speaking,  $s_1$  in these formulæ denotes the *mean* specific heat of the first substance between the temperatures  $t_1$  and  $t$ ,  $s_2$  the mean specific heat of the second substance between  $t_2$  and  $t$ , and so on.

It is not necessary to suppose the two bodies to be literally *mixed*. One of them may be a solid and the other a liquid in which it is plunged. The formulæ apply whenever bodies at different temperatures are reduced to a common temperature by interchange of heat one with another.

**64. Practical Application.**—The following is an outline of the method most frequently employed for determining the specific heats of solid bodies.

The body to be tested is raised to a known temperature  $t_1$ , and then plunged into water of a known temperature  $t_2$  contained in a thin copper vessel called a *calorimeter*. If  $m_1$  be the mass of the body,  $m_2$  that of the water before immersion, and  $t$  the final temperature, all of which are directly observed, we have

$$m_1 s_1 (t_1 - t) = m_2 (t - t_2), \quad (5)$$

since  $s_2$ , the specific heat of the water, may be taken as unity. Hence we have

$$s_1 = \frac{m_2 (t - t_2)}{m_1 (t_1 - t)}. \quad (6)$$

**65. Corrections.**—The theoretical conditions which are assumed in the above calculation, cannot be exactly realized in practice.

I. The calculation assumes that the only exchange of heat is between the body and the water, which is not actually the case; for

1. The body is often contained in an envelope which cools along with it, and thus furnishes part of the heat given up.

2. The heat is not given up exclusively to the water, but partly to the calorimeter itself, to the thermometer, and to such other instruments as may be employed in the experiment, as, for instance, a rod to stir the liquid for the purpose of establishing uniformity of temperature throughout it.

In order to take account of these disturbing circumstances, it is only necessary to know the thermal capacity of each of the bodies which takes part in the exchange of heat. We shall then have such an equation as the following:—

$$(m_1 s_1 + c_1) (t_1 - t) = (m_2 + c_2 + c_3 + c_4) (t - t_2),$$

where  $c_1$  denotes the thermal capacity of the envelope, and  $c_2, c_3, c_4$  are the thermal capacities of the calorimeter, thermometer, and stirring rod.

II. The calorimeter gives out heat to the surrounding air, or takes heat from it. This difficulty is often met by contriving that the heat gained by the calorimeter from the air in the first part of the experiment shall be as nearly as possible equal to that which it loses to the air in the latter part.

This condition will be fulfilled if the average temperature of the calorimeter (found by taking the mean of numerous observations at equal small intervals of time) is equal to the temperature of the air. As the immersed body gives out its heat to the water very rapidly at first, and then by degrees more and more slowly, the initial defect of temperature must be considerably greater than the final excess, to make the compensation exact.

Instead of attempting exact compensation, some observers have determined, by a separate experiment, the rate at which interchange of heat takes place between the calorimeter and the air, when there is a given difference of temperature between them. This can be observed by filling the calorimeter with water in which a thermometer is immersed. The rate of interchange is almost exactly proportional to the difference of temperature between the calorimeter and the air, and is independent of the nature of the contents. The law of interchange having thus been determined, the temperature of the calorimeter must be observed at stated times during the progress of the experiment on specific heat; the total heat lost or gained by interchange with the air will thus be known, and this total heat divided by the total thermal capacity of the calorimeter and its contents gives a correction, which is to be added to or subtracted from  $t$  the observed final temperature.

66. *Regnault's Apparatus.*—The subject of specific heat has been investigated with great care by Regnault, who employed for that purpose an apparatus in which the advantages of convenience and precision are combined. The body whose specific heat is required is divided into small fragments, which are placed in a cylindrical basket G (Fig. 44) of very fine brass wire, in the centre of which

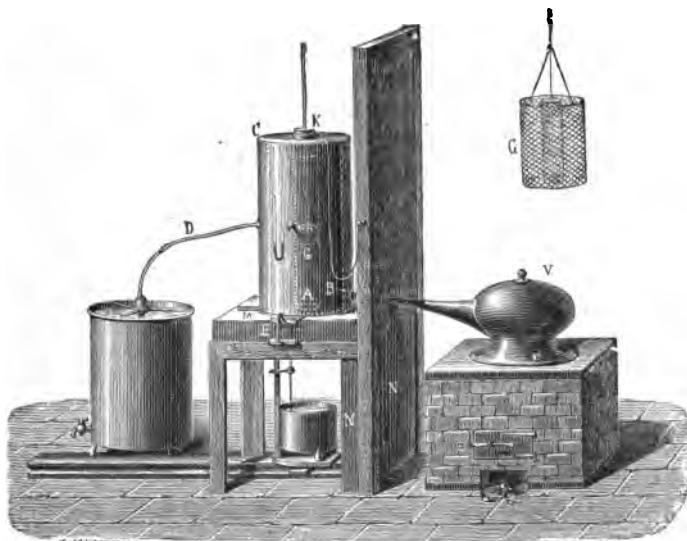


Fig. 44.—Regnault's Apparatus.

is a tube of the same material for the insertion of a thermometer. The basket is shown separately in the figure on a larger scale than the rest of the apparatus. This basket is suspended in the central compartment of the steamer A B C, the suspending thread being fixed by the cork K, through which the stem of the thermometer passes. The steamer consists of three concentric cylinders, the two outer compartments being occupied by steam, which is supplied from the boiler V to the second compartment, and finally escapes from the outermost compartment through the tube D into a condenser. In the bottom of the steamer are a pair of slides E which can be drawn out when required.

The steamer rests, by means of a sheet of cork, upon a hollow metal vessel M N, consisting of a horizontal portion M and a vertical portion N, filled with cold water, and serving as a screen for the calorimeter; the horizontal portion, and the cork above it,

having a hole in the centre large enough for the basket G to pass through.

The calorimeter itself, which is shown beneath the steamer in the figure, is a vessel of very thin polished brass, resting by three points upon a small wooden sled, which runs smoothly along a guiding groove. The thermometer for measuring the temperature of the water in the calorimeter, is carried by a support attached to the sled.

The basket, with its contents, is left in the steamer until the temperature indicated by the thermometer has been for some time stationary. The calorimeter, which, up to this time has been kept as far away as it can slide, is then pushed into the position shown in the figure, the slides E, which close the bottom of the compartment in which the basket is, are drawn out; and the cork at the top having been loosened, the basket is lowered by its supporting thread into the calorimeter, which is immediately slid back to its former place. The basket is then moved about in it until the water attains its maximum temperature, which is read off on the thermometer.

To determine the specific heats of liquids, a thin glass tube is employed instead of the basket. It is nearly filled with the liquid and hermetically sealed.

For solids which are soluble in water, or upon which water has a chemical action, some other liquid—oil of turpentine, for example—is placed in the calorimeter, instead of water; and the experiment is in other respects the same.

The specific heats of several substances are given in the following table:—

Water, . . . . . 1·00000

SOLIDS.

Antimony, . . . . .	0·05077	Brass, . . . . .	0·09391
Silver, . . . . .	0·05601	Nickel, . . . . .	0·10860
Arsenic, . . . . .	0·08140	Gold, . . . . .	0·03244
Bismuth, . . . . .	0·03084	Phosphorus, . . . . .	0·18870
Cadmium, . . . . .	0·05669	Platinum, . . . . .	0·03243
Charcoal, . . . . .	0·24150	Lead, . . . . .	0·03140
Copper, . . . . .	0·09215	Plumbago, . . . . .	0·21800
Diamond, . . . . .	0·14680	Sulphur, . . . . .	0·20259
Tin, . . . . .	0·05623	Glass, . . . . .	0·19768
Iron, . . . . .	0·11379	Zinc, . . . . .	0·09555
Iodine, . . . . .	0·05412	Ice, . . . . .	0·5040

LIQUIDS.

Mercury, . . . . .	0·03332	Benzine, . . . . .	0·3952
Acetic acid, . . . . .	0·6589	Ether, . . . . .	0·6157
Alcohol at 36°, . . . . .	0·6735	Oil of turpentine, . . . . .	0·4629

**67. Great Specific Heat of Water.**—This table illustrates the important fact, that, of all substances, water has the greatest specific heat; that is to say, it absorbs more heat in warming, and gives out more heat in cooling, through a given range of temperature, than an equal weight of any other substance. The quantity of heat which raises a pound of water from  $0^{\circ}$  to  $100^{\circ}$  C. would suffice to raise a pound of iron from  $0^{\circ}$  to about  $900^{\circ}$  C., that is to a bright red heat; and conversely, a pound of water in cooling from  $100^{\circ}$  to  $0^{\circ}$ , gives out as much heat as a pound of iron in cooling from  $900^{\circ}$  to  $0^{\circ}$ . This property of water is utilized in the heating of buildings by hot water, and in other familiar instances, such as the bottles of hot water used for warming beds, and railway foot-warmers.

**68. Ice Calorimeters.**—In the calorimeters above described, the heat which a body loses in cooling is measured by the elevation of temperature which it produces in a mass of water. In ice calorimeters this heat is measured by the quantity of ice (initially at the freezing-point) which it melts. In some ice calorimeters the water produced by melting is collected and weighed; in Bunsen's, the measurement depends upon the diminution of volume which occurs when ice melts.

The construction of this instrument is shown in Fig. 45. The small thin test-tube A, open to the air at the top, is sealed into the reservoir B, which communicates with the tube C having at its end a movable plug D, through which passes the vertical portion of a fine tube S, whose other portion is horizontal and may be of considerable length. The small body whose specific heat is required is heated, and dropped into ice-cold water which stands at the level  $\alpha$  in A. The surrounding space in the reservoir, from the level  $\beta$  to the top, contains ice and ice-cold water, and some of the ice is melted by the heat emitted from the body in A, the whole apparatus being kept immersed in a mixture of ice and water to prevent loss or gain of heat externally. The diminution in the joint volume of water and ice in B produced by the melting is indicated by the movement of the end of a mercurial column in the horizontal part of S, the whole space from B to S being occupied by mercury.

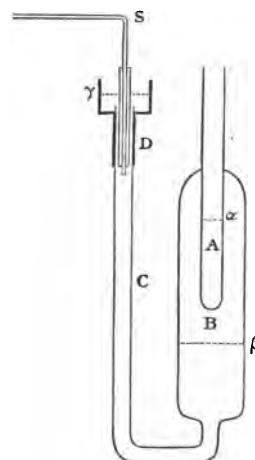


Fig. 45.—Bunsen's Calorimeter.

To prevent the formation of air bubbles in the reservoir B, it is filled with boiling water, which is afterwards frozen. The mercury should also be boiled to expel air, and before its introduction the tubes should be thoroughly dried.

The graduation of the tube S on which the indications are read may be arbitrary, and the value of the divisions is determined by observing the effect of a known mass of water at a known temperature when introduced into A. By means of the sliding plug D, the end of the column can be brought to a convenient part of the tube before each experiment.

69. **Specific Heats of Gases.**—Regnault made very careful determinations of the specific heats of air and other gases, by means of an apparatus in which a measured quantity of gas at a known temperature was passed through a series of spiral tubes surrounded by cold water, and finally escaped at a temperature sensibly the same as that of the water. The elevation produced in the temperature of the water by this process, furnished a measure of the quantity of heat given out by the gas in falling through a known range of temperature. The gas had sensibly the same pressure on entering as on leaving the calorimeter; the specific heat determined by the experiments was therefore the specific heat *at constant pressure*. This element must be carefully distinguished from the specific heat of a gas *at constant volume*. The connection between the two will be discussed in a later chapter.

Regnault's experiments established the following conclusions.

(1) The specific heat of a gas is the same at all pressures; in other words, the thermal capacity per unit volume is directly as the density.

(2) The specific heats of different simple gases are approximately in the inverse ratio of their relative densities.

Let  $s$  denote the specific heat and  $d$  the absolute density of a gas at a given pressure and temperature; then this law asserts that the product  $sd$  is the same (approximately) for all simple gases. But since  $d$  is the mass of unit volume,  $sd$  is the capacity of unit volume. The law may therefore be thus expressed:—

*All simple gases have approximately the same thermal capacity per unit volume, when compared at the same pressure and temperature.*

(3) The specific heat of a gas is the same at all temperatures, temperature being measured by the air-thermometer, or by the expansion

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of the gas itself at constant pressure. This is equivalent to the assertion that *if equal quantities of heat be successively added to a gas at constant pressure, the volume of the gas will increase in arithmetical progression.* We here neglect the slight differences which exist between the expansions of different gases, and also their slight departures from Boyle's law.

The specific heat of dry air (at constant pressure) according to Regnault is .2375.

The three laws above stated are also true for the specific heat of gases *at constant volume.* The third law may then be stated in the following form:—

*If equal quantities of heat be successively added to a gas at constant volume, the pressure will increase in arithmetical progression.*

**70. Dulong and Petit's Law.**—According to the modern molecular theory of gases, all simple gases at the same pressure and temperature have the same number of atoms per unit volume. The mass of an atom of any gas will therefore be proportional to the relative density of the gas, and law (2) of last section will reduce to the following:—The specific heats of different simple gases are inversely as the masses of their atoms.

The second statement of the same law assumes the following still more simple form:—

*An atom of one gas has the same thermal capacity as an atom of any other gas.*

What is called in chemistry the *atomic weight* of an elementary substance is proportional to the supposed mass of an atom of the substance, and is believed to be proportional to the relative density of the substance when reduced to a state of vapour at high temperature and low pressure.

It was remarked by Dulong and Petit that the specific heats of elementary substances are for the most part in the inverse ratio (approximately) of their atomic weights; or the *product of specific heat and atomic weight is (approximately) constant.* The constancy is very rough when the specific heats are taken at ordinary temperatures; but it is probable that at very high temperatures the law would be nearly exact.

**71. Method of Cooling.**—Attempts have sometimes been made to compare the specific heats of different substances by means of the times which they occupy in cooling through the same range. If

two exactly similar thin metallic vessels are filled with two different substances, and after being heated to a common temperature are allowed to cool in air under the same conditions, the times which they occupy in falling to any other common temperature will be proportional to the quantities of heat which they emit, if we can assume that the contents of the vessels are at sensibly the same temperatures as their surfaces. We have thus a comparison of the thermal capacities of the two substances per unit volume.

In the case of solid substances, their differences in conducting power render the method worthless; but Regnault has found that it gives tolerably correct results in the case of liquids. In fact the extreme mobility of liquids, combined with their expansion when heated, prevents any considerable difference of temperature from existing in the same horizontal layer; so that the centre is sensibly at the same temperature as the circumference.

## CHAPTER VII.

### FUSION AND SOLIDIFICATION.

**72. Fusion.**—Many solid bodies, when raised to a sufficiently high temperature, become liquid. This change of state is called *melting* or *fusion*, and the temperature at which it occurs (called the melting-point, or temperature of fusion) is constant for each substance, with the exception of the variations—which in ordinary circumstances are insignificant—due to differences of pressure (§ 86). The melting-points of several substances are given in the following table:—

TABLE OF MELTING-POINTS, IN DEGREES CENTIGRADE.

Mercury, . . . . .	-39	Tin, . . . . .	230
Ice, . . . . .	0	Bismuth, . . . . .	262
Butter, . . . . .	33	Lead, . . . . .	326
Lard, . . . . .	33	Zinc, . . . . .	412
Spermaceti, . . . . .	49	Antimony, . . . . .	432
Stearine, . . . . .	55	Aluminium, . . . . .	600
Yellow Wax, . . . . .	62	Bronze, . . . . .	900
White Wax, . . . . .	68	Pure Silver, . . . . .	954
Stearic Acid, . . . . .	70	Gold, . . . . .	1045
Phosphorus, . . . . .	44	Copper, . . . . .	1054
Potassium, . . . . .	63	Cast Iron, . . . . .	1050 to 1250
Sodium, . . . . .	95	Steel, . . . . .	1300 to 1400
Iodine, . . . . .	107	Wrought Iron, . . . . .	1500 to 1600
Sulphur, . . . . .	110	Platinum, . . . . .	1775

Some bodies, such as charcoal, have hitherto resisted all attempts to reduce them to the liquid state; but this is to be attributed only to the insufficiency of the means which we are able to employ.

It is probable that, by proper variations of temperature and pressure, all simple substances, and all compound substances which would not be decomposed, could be compelled to assume the three forms, solid, liquid, and gaseous.

The passage from the solid to the liquid state is generally abrupt;

but this is not always the case. Glass, for instance, before reaching a state of perfect liquefaction, passes through a series of intermediate stages in which it is of a viscous consistency, and can be easily drawn out into exceedingly fine threads, or moulded into different shapes.

**73. Definite Temperature.**—When the solid and liquid forms of a substance are present in contact with each other in the same vessel, and time is allowed for uniformity of temperature to be established; the temperature will be that of the melting-point, and will be quite independent of the relative proportions of solid and liquid in the vessel. For example, water and ice, in any proportions, if brought to a uniform temperature, will be at 0° C.

It is sometimes stated that, if heat be applied to a vessel containing ice and water, the temperature of the contents will remain at 0° C. till all the ice is melted; but this statement is not strictly accurate. The portions of the water in contact with the sides and receiving heat from the sides, will be at a somewhat higher temperature than the portions in contact with the ice. If, however, the application of heat be stopped, and uniformity of temperature be established through the whole mass, by stirring or otherwise, the temperature of the whole will then be 0° C.

For each substance that passes, like ice, by a sudden transition, from the solid to the liquid state, without an intermediate pasty condition, there is one definite temperature at which the solid and the liquid forms can exist in contact under atmospheric pressure. This temperature is variously styled the *temperature of fusion*, the *melting-point*, and the *freezing-point*.

**74. Latent Heat of Fusion.**—Although the solid and liquid forms of a substance can exist together at the same temperature, the application of heat is requisite for reducing the solid to the liquid form. If ice at 0° C. be put into a vessel and placed on the fire, it will be gradually melted by the heat which it receives from the fire; but at any time during the operation, if we stop the application of heat, and stir the contents till uniformity of temperature is established, the temperature will be 0° C. as at first. The heat which has been received has left its effect in the shape of the melting of ice, not in the shape of rise of temperature. Heat thus spent is usually called *latent heat*, a name introduced by Black, who was the first to investigate this subject. A similar absorption of heat without rise of temperature occurs when a boiling liquid is converted into vapour. Hence it is necessary to distinguish between the *latent heat of fusion*

and the *latent heat of vaporization*. The former is often called the latent heat of the liquid, and the latter of the vapour. Thus we speak of the latent heat of water (which becomes latent in the melting of ice), and of the latent heat of steam (which becomes latent in the vaporization of water).

The same amount of heat which is absorbed in the conversion of the solid into the liquid, is given out when the liquid is converted into the solid; and a similar remark applies to the conversion of vapour into liquid.

**75. Measurement of Heat of Fusion.**—The heat required to convert unit mass of a substance from the solid to the liquid form is employed as the measure of the latent heat of liquefaction of that substance. Its amount for several substances is given in the last column of the following table:—

Substances.	Melting-point.	Specific Heats		Latent Heat of Fusion.
		In the Solid State.	In the Liquid State.	
Ice, . . . . .	0°	.5040	1.0000	79.250
Phosphorus, . . .	44.20	.2000	.2000	5.400
Sulphur, . . .	111	.2020	.2340	9.368
Bromine, . . .	-7.32	.0840	.1870	16.185
Tin, . . . .	232	.0560	.0640	14.252
Bismuth, . . . .	266	.0308	.0363	12.640
Lead, . . . .	326	.0314	.0402	5.369
Mercury, . . . .	-39	.0319	.0333	2.820

The most accurate determinations of latent heat of fusion have been made by a method similar to the "method of mixtures" which is employed in the determination of specific heats.

Let  $i$  grammes of ice at  $0^\circ$  be mixed with  $w$  grammes of water at  $t^\circ$ , and when all the ice is melted let the temperature of the whole be  $\theta^\circ$ . Then if the specific heat of water at all temperatures between  $0^\circ$  and  $t^\circ$  can be taken as unity, we have  $w(t - \theta)$  units of heat lost by the  $w$  grammes of water, and spent partly in melting the ice, and partly in raising the temperature of the water produced by the melting from  $0^\circ$  to  $\theta^\circ$ . Hence if  $x$  denote the latent heat of liquefaction, we have

$$w(t - \theta) = i(x + \theta);$$

whence we find

$$x = \frac{wt}{i} - \frac{w + i}{i}\theta.$$

One gramme of water at between  $79^\circ$  and  $80^\circ$ , or between  $79$  and  $80$

grammes of water at  $1^\circ$ , will be just enough to melt one gramme of ice at  $0^\circ$ ; and the final temperature of the whole will in each case be  $0^\circ$ .

For any other substance, let  $T^\circ$  be the melting-point,  $s$  the specific heat of the substance in the liquid form, and  $x$  the latent heat of liquefaction. Then if  $i$  grammes of the solid at  $T^\circ$  be mixed with  $w$  grammes of the liquid at  $t^\circ$ , and  $\theta^\circ$  be the temperature of the whole when all the solid is melted, we have

$$sw(t - \theta) = ix + i(\theta - T);$$

whence

$$x = \frac{w}{i} s(t - \theta) - (\theta - T).$$

In these calculations we have tacitly assumed that no heat is gained or lost externally by the substance under examination. Practically, it is necessary (as in the determination of specific heats) to take account of the thermal capacity of the calorimeter (that is the vessel in which the substance is contained) and of the heat gained or lost by the calorimeter to surrounding bodies. For substances which have a high melting-point, a different method may be employed. The body in the molten state may be inclosed in a small thin metal box and immersed in the water of the calorimeter. Let  $m$  be the mass of the body,  $T'$  its initial temperature,  $T$  its melting-point,  $s'$  its specific heat in the liquid, and  $s$  in the solid state,  $\theta$  the final temperature of the calorimeter, and  $x$  the latent heat of the substance, which is required; then the heat lost by the body is

$$m s'(T' - T) + m x + m s(T - \theta),$$

and this quantity, together with the heat lost by the envelope must be equated to the heat gained by the calorimeter and its original contents, subject to a correction for radiation which can be determined by the ordinary methods.

As regards the two specific heats which enter this equation,  $s$  the specific heat in the solid state may be regarded as known, and  $s'$  the specific heat in the liquid state can be deduced by combining this equation with another of the same kind in which the initial temperature is very different. In the case of bodies which, like mercury and bromine, are liquid at ordinary temperatures, the specific heat in the solid state can be found by a similar but inverse process.

**76. Conservatism of Water.**—The table in § 75 shows that the

heat of fusion is much greater for ice than for any of the other substances mentioned. It is 14 times as great as for lead, and 28 times as great as for mercury. Ice is, in this sense, the most difficult to melt, and water the most difficult to freeze, of all substances; a fact which is of great importance in the economy of nature, as tending to retard the processes both of freezing and thawing. Even as it is, the effects of a sudden thaw are often disastrous; and yet, for every particle of ice melted, as much heat is required as would raise the water produced through  $79^{\circ}$  C. or  $142^{\circ}$  F.

**77. Solution.**—The reduction of a body from the solid to the liquid state may be effected by other means than by the direct action of heat; it may be produced by the action of a liquid. This is what occurs when, for instance, a grain of salt or of sugar is placed in water; the body is said to be *dissolved* in the water. Solution, like fusion, is accompanied by the disappearance of heat consequent on the change from the solid to the liquid state. For example, by rapidly dissolving nitrate of ammonia in water, a fall of from  $20^{\circ}$  to  $25^{\circ}$  C. can be obtained.

Unlike fusion, it is attached to no definite temperature, but occurs with more or less freedom over a wide range. Rise of temperature usually favours it; but there are some strongly marked exceptions.

**78. Freezing-mixtures.**—The absorption of heat which accompanies the liquefaction of solids is the basis of the action of freezing-mixtures. In all such mixtures there is at least one solid ingredient which, by the action of the rest, is reduced to the liquid state, thus occasioning a fall of temperature proportional to the latent heat of its liquefaction.

The mixture most commonly employed in the laboratory is one of snow and salt. There is a double absorption of heat caused by the simultaneous melting of the snow and dissolving of the salt. Professor Guthrie found that the proportions of the two ingredients and their initial temperatures may vary between very wide limits without affecting the temperature obtained. This definite temperature is the freezing-point of a definite compound of salt and water. When ordinary sea-water in a vessel is subjected to cold, the ice first formed is fresh; and the brine increases in strength by the freezing out of the water till it has attained the strength of the definite compound above mentioned. Then a change occurs, and the ice formed is no longer fresh, but of the same composition as the brine. From this point onward until all the brine is frozen the temperature of

the liquid is  $-22^{\circ}$  C., which is, accordingly, the temperature obtained by mixing snow and salt.<sup>1</sup>

Fahrenheit intended that the temperature thus obtained should be the zero of his scale, the freezing-point of water being  $32^{\circ}$  and the boiling-point  $212^{\circ}$ ; but the thermometers with which he worked were extremely rough, and if we define his scale by the two ordinary fixed points, the temperature  $-22^{\circ}$  C. will not be  $0^{\circ}$  F., but  $-7.6^{\circ}$  F.

79. The following mixtures are also sometimes employed.

	Proportions by Weight.	Fall of Tempera- ture Produced.
Snow,	3	
Crystallized Chloride of Calcium,	4	from $0^{\circ}$ to $-48^{\circ}$ .
Nitrate of Ammonia,	1	
Water,	1	from $+10^{\circ}$ to $-15^{\circ}$ .
Sal-ammoniac,	5	
Nitrate of Potash,	5	
Sulphate of Soda,	8	from $+10^{\circ}$ to $-15^{\circ}$ .
Water,	16	
Sulphate of Soda,	8	from $+10^{\circ}$ to $-17^{\circ}$ .
Hydrochloric Acid,	5	

Fig. 46 represents an apparatus intended for the artificial production of ice. The water to be frozen is inclosed in a mould formed of two concentric vessels—an arrangement which has the advantage

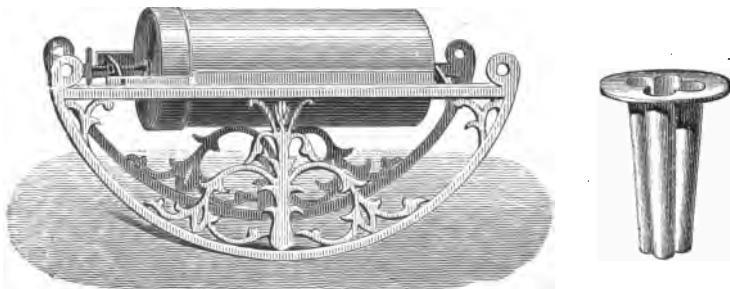


Fig. 46.—Freezing Rocker.

of giving a large surface of contact; and the mould is immersed in the freezing-mixture (hydrochloric acid and sulphate of soda) which is contained within a metal cylinder mounted on a cradle, the rocking of which greatly assists the operation.

80. **Solidification or Congelation.**—All liquids are probably capable of being solidified; though some of them, for example, alcohol and bisulphide of carbon, have never yet been seen in the solid state.

<sup>1</sup> *Proceedings of Physical Society of London*, January, 1875, p. 78.

The temperature of fusion is the highest temperature at which congelation can occur, and is frequently called the *temperature of congelation* (or the *freezing-point*); but it is possible to preserve substances in the liquid state at lower temperatures. Liquids thus cooled below their so-called freezing-points have, however, if we may so say, a *tendency to freeze, which is only kept in check by the difficulty of making a commencement*. If freezing once begins, or if ever so small a piece of the same substance in the frozen state be allowed to come in contact with the liquid, congelation will quickly extend until there is none of the liquid left at a temperature below that of fusion. The condition of a liquid cooled below its freezing-point has been aptly compared to that of a row of bricks set on end in such a manner that if the first be overturned, it will cause all the rest to fall, each one overturning its successor.

The contact of its own solid infallibly produces congelation in a liquid in this condition, and the same effect may often be produced by the contact of some other solid, especially of a crystal, or by giving a slight jar to the containing vessel.

Despretz has cooled water to  $-20^{\circ}$  C. in fine capillary tubes, without freezing, and Dufour has obtained a similar result by suspending globules of water in a liquid of the same specific gravity with which it would not mix, this liquid being one which had a very low freezing-point.

**81. Heat set free in Congelation.**—At the moment when congelation takes place, the thermometer immediately rises to the temperature of the melting-point. This may be easily shown by experiment. A small glass vessel is taken, containing water, in which a mercurial thermometer is plunged. By means of a frigorific mixture the temperature is easily lowered to  $-10^{\circ}$  or  $-12^{\circ}$ , without the water freezing; a slight shock is then given to the glass, congelation takes place, and the mercury rises to  $0^{\circ}$ .

The quantity of ice that will be formed when congelation sets in, in water which has been cooled below the freezing-point, may be computed—very approximately at least—in the following way:—

Suppose we have unit mass of water at the temperature  $-t^{\circ}$ , and when congelation sets in suppose that it yields a mass  $x$  of ice and a mass  $1-x$  of water, both at  $0^{\circ}$ .

To melt this ice and bring the whole mass to the state of water at  $0^{\circ}$  would require the addition of  $79.25x$  units of heat; but to bring the whole mass of water from  $-t$  to  $0^{\circ}$  would require  $t$  units of heat.

These two quantities of heat must be the same, subject to a possible correction which will be discussed in the chapter on thermodynamics. Hence we may write

$$79.25x = t; \quad x = \frac{t}{79.25}.$$

Whatever the original quantity of water may be, this value of  $x$  expresses the fraction of it which will be converted into ice.

**82. Crystallization.**—When the passage from the liquid to the solid state is a gradual one, it frequently happens that the molecules group themselves in such a manner as to present regular geometric forms. This process is called crystallization, and the regular bodies thus formed are called crystals. The particular crystalline form assumed depends upon the substance, and often affords a means of recognizing it. The forms, therefore, in which bodies crystallize are among their most important characteristics, and are to some extent analogous to the shapes of animals and plants in the organic world.

In order to make a body crystallize in solidifying, the following method is employed. Suppose the given body to be bismuth; the first step is to melt it, and then leave it to itself for a time. The metal begins to solidify first at the surface and at the sides, where it is most directly exposed to cooling influences from without; accordingly, when the outer layer of the metal is solidified, the interior is still in the liquid state. If the upper crust be now removed, and the liquid bismuth poured off, the sides of the vessel will be seen to be covered with a number of beautiful crystals.

If the metal were allowed to stand too long, the entire mass would become solid, the different crystals would unite, and no regularity of structure would be observable.

**83. Flowers of Ice.**—The tendency of ice to assume a crystalline form is seen in the fern-leaf patterns which appear on the windows in winter, caused by the congealing of moisture on them, and still more distinctly in the symmetrical forms of snow-flakes (see Chap. xi.). In a block of ice, however, this crystalline structure does not show itself, owing to the closeness with which the crystals fit into each other, so that a mass of this substance appears almost completely *amorphous*. Tyndall, however, in a very interesting experiment, succeeded in gradually *decry stallizing* ice, if we may use the expression, and thus exhibiting the crystalline elements of which it is composed. The experiment consists in causing a pencil of solar rays

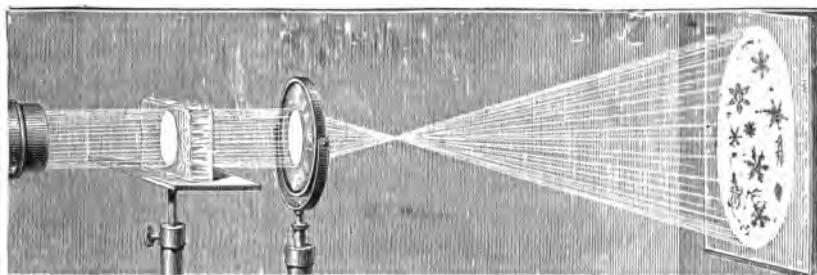


Fig. 47.—Flowers of Ice projected on a Screen.

to fall perpendicularly to the surfaces of congelation on a sheet of ice, such as is naturally formed upon the surface of water in winter. A lens placed behind the ice (Fig. 47) serves to project upon a screen the image of what is found in the interior of the block.

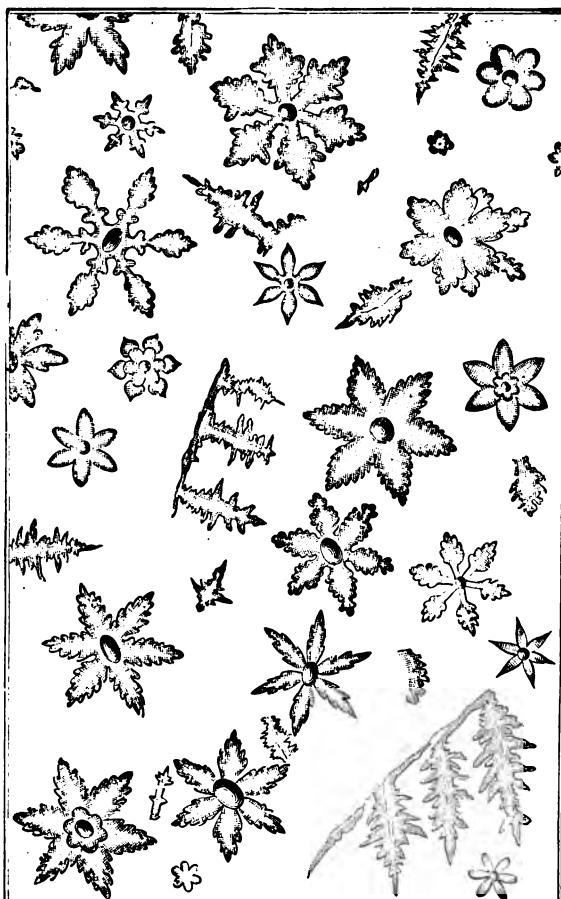


Fig. 48.—Flowers of Ice.

The successive appearances observed upon the screen are shown in Fig. 48. A small luminous circle is first seen, from which branch out rays, resembling the petals of a flower whose pistil is the circle. Frequent changes also occur in the shape of the branches themselves, which are often cut so as to resemble fern-

leaves, like those seen upon the windows during frost. In this experiment, the solar heat, instead of uniformly melting the mass of ice, which it would certainly do if the mass were amorphous, acts successively upon the different crystals of which it is built up, affecting them in the reverse order of their formation. There are thus produced a number of spaces of regular shape, containing water, and producing comparatively dark images upon the screen. In the centre of each there is generally a bright spot, which corresponds to an empty space, depending on the fact that the water occupies a smaller volume than the ice from which it has been produced.

**84. Supersaturation.**—The proportion of solid matter which a liquid can hold in solution varies according to the temperature; and as a general rule, though not by any means in all cases, it increases as the temperature rises. Hence it follows, that if a saturated solution be left to itself, the effect of evaporation or cooling will be gradually to diminish the quantity of matter which can be held in solution. A portion of the dissolved substance will accordingly pass into the solid state, assuming generally a crystalline form. This is an exceedingly common method of obtaining crystals, and is known as the *humid way*.

In connection with this process a phenomenon occurs which is precisely analogous to the cooling of a liquid below its freezing-point. It may be exemplified by the following experiment.

A tube drawn out at one end (Fig. 49) is filled with a warm concentrated solution of sulphate of soda. The solution is boiled, and while ebullition is proceeding freely, the tube is hermetically sealed; by this means the tube is exhausted of air. The solution when



Fig. 49.—Preparation of Supersaturated Solution of Sulphate of Soda.

left to itself cools without the solid being precipitated, although the liquid is *supersaturated*. But if the end of the tube be broken off, and the air allowed to enter, crystallization immediately commences at the surface, and is quickly propagated through the whole length of the tube; at the same time, as we should expect, a considerable rise of temperature is observed. If the phenomenon does not at once occur on the admission of the air, it can be produced with certainty by throwing a small piece of the solid sulphate into the solution.

**85. Change of Volume at the Moment of Congelation. Expansive Force of Ice.**—In passing from the liquid to the solid state, bodies generally undergo a diminution of volume; there are, however, exceptions, such as ice, bismuth, and cast-iron. It is this property which renders this latter substance so well adapted for the purposes of moulding, as it enables the metal to penetrate completely into



Fig. 50.—Bursting of Iron Tube by Expansion of Water in Freezing.

every part of the mould. The expansion of ice is considerable, amounting to about  $\frac{1}{2}$ ; its production is attended by enormous

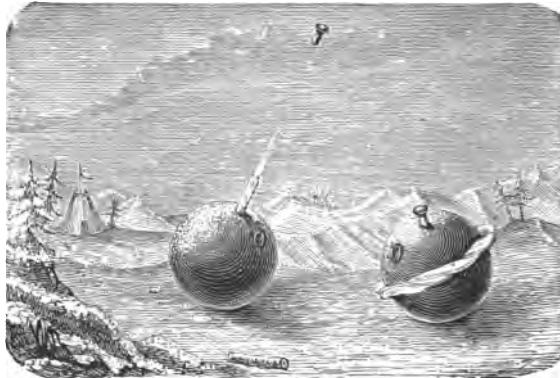


Fig. 51.—Experiment of Major Williams.

mechanical force, just as in the analogous case of expansion by heat.

Its effect in bursting water-pipes is well known. The following experiment illustrates this expansive force. A tube of forged iron (Fig. 50) is filled with water, and tightly closed by a screw-stopper. The tube is then surrounded with a freezing-mixture of snow and

salt. After some time the water congeals, a loud report is often heard, and the tube is found to be rent.

The following experiment, performed by Major Williams at Quebec, is still more striking. He filled a 12-inch shell with water and closed it with a wooden stopper, driven in with a mallet. The shell was then exposed to the air, the temperature being  $-28^{\circ}$  C. ( $-18^{\circ}$  F.). The water froze, and the bung was projected to a distance of more than 100 yards, while a cylinder of ice of about 8 inches in length was protruded from the hole. In another experiment the shell split in halves, and a sheet of ice issued from the rent (Fig. 51).

It is the expansion and consequent lightness of ice which enables it to float upon the surface of water, and thus afford a protection to animal life below.

**86. Effect of Pressure on the Melting-point.**—Professor James Thomson was led by theoretical considerations to the conclusion that, in the case of a substance which, like water, expands in solidifying, the freezing (or melting) point must of necessity be lowered by pressure, and that a mixture of ice and ice-cold water would fall in temperature on the application of pressure. His reasoning<sup>1</sup> consisted in showing that it would otherwise be possible (theoretically at least) to construct a machine which should be a perpetual source of work without supply; that is, what is commonly called a perpetual motion.

The matter was shortly afterwards put to the test of experiment by his brother, Lord Kelvin, who compressed, in an Ørsted's piezometer, a mixture of ice and water, in which was inserted a very delicate thermometer protected from pressure in the same manner as the instrument represented in Fig. 15 (§ 12). The thermometer showed a regular fall of temperature as pressure was applied, followed by a return to  $0^{\circ}$  C. on removing the pressure. Pressures of 8·1 and 16·8 atmospheres (in excess of atmospheric pressure) lowered the freezing-point by ·106 and ·232 of a degree Fahr. respectively as indicated by the thermometer, results which agree almost exactly with Prof. J. Thomson's prediction of ·0075 of a degree Cent., or ·0135 of a degree Fahr. per atmosphere.

Mousson has since succeeded in reducing the melting-point several degrees by means of enormous pressure. He employed two forms of apparatus, by the first of which he melted ice at the temperature of  $-5^{\circ}$  C., and kept the water thus produced for a considerable time

<sup>1</sup> *Transactions Royal Society, Edinburgh.* January, 1849.—*Cambridge and Dublin Math. Journal.* November, 1850.

at this temperature. This apparatus had windows (consisting of blocks of glass) in its sides, through which the melting of the ice

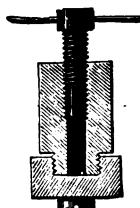


Fig. 52.  
Mousson's  
Apparatus.

was seen. His second form of apparatus, which bore a general resemblance to the first, is represented in the annexed figure. It consisted of a steel prism with a cylindrical bore, having one of its extremities closed by a conical stopper strongly screwed in, the rest of the bore being traversed by a screw-piston of steel. The apparatus was inverted, and nearly filled with water recently boiled, into which a piece of copper was dropped, to serve as an index. The apparatus, still remaining in the inverted position, was surrounded by a freezing-mixture, by means of which the water was reduced to ice at the temperature of  $-18^{\circ}$  C. The stopper was then screwed into its place, and the apparatus placed in the erect position. The piston was then screwed down upon the ice with great force, the pressure exerted being estimated in some of the experiments at several thousand atmospheres. The pressure was then relaxed, and, on removing the stopper, the copper index was found to have fallen to the bottom of the bore, showing that the ice had been liquefied.

Experiments conducted by Bunsen and by Hopkins have shown that wax, spermaceti, sulphur, stearin, and paraffin—substances which, unlike ice, expand in melting—have their melting points raised by pressure, a result which had been predicted by Lord Kelvin.

**87. Effect of Stress in general upon Melting and Solution.**—In the experiments above described, the pressure applied was hydrostatical, and was therefore equal in all directions. But a solid may be exposed to pressure in one direction only, or to pull in one or more directions, or it may be subjected to shearing, twisting, or bending forces, all these being included under the general name of *stress*.

Reasoning, based on the general laws of energy, leads to the conclusion that stress of any kind other than hydrostatic, applied to a solid, must lower its melting-point. To quote Professor J. Thomson (*Proc. Roy. Soc.* Dec. 1861), "Any stresses whatever, tending to change the form of a piece of ice in ice-cold water, must impart to the ice a tendency to melt away, and to give out its cold, which will tend to generate, from the surrounding water, an equivalent quantity of ice free from the applied stresses," and "stresses tending to change the form of any crystals in the saturated solutions from which they have

been crystallized must give them a tendency to dissolve away, and to generate, in substitution for themselves, other crystals free from the applied stresses or any equivalent stresses."<sup>1</sup> This conclusion he verified by experiments on crystals of common salt. He at the same time suggested, as an important subject for investigation, the effect of hydrostatic pressure on the crystallization of solutions, a subject which was afterwards taken up experimentally by Sorby, who obtained effects analogous to those above indicated as occurring in connection with the melting of ice and wax.

**88. Bottomley's Experiment.**—Mr. J. T. Bottomley has devised an instructive experiment on the effect of applying stress to ice. A block of ice is placed on two supports with a little space between them, and a stout copper wire with heavy weights at its two ends is slung across it. The wire gradually makes its way through the block—occupying, perhaps, an hour or two in its passage—and at last drops upon the floor; but the block is not cut in two; the cut which the wire makes is filled up by the formation of fresh ice as fast as the wire advances. The pressure of the wire lowers the melting-point of the ice in front, and causes it to melt at this lowered melting-point. The wire itself acquires, by contact with the melting ice, a temperature below zero, and the escaping water freezes at the back of the wire.

**89. Regelation of Ice.**—Faraday in 1850 called attention to the fact that pieces of moist ice placed in contact with one another will freeze together even in a warm atmosphere. This phenomenon, to which Tyndall has given the name of *regelation*, admits of ready explanation by the principles just enunciated. Capillary action at the boundaries of the film of water which connects the pieces placed in contact, produces an effect equivalent to attraction between them, just as two plates of clean glass with a film of water between them seem to adhere. Ice being wetted by water, the boundary of the connecting film is concave, and this concavity implies a diminution of pressure in the interior. The film, therefore, exerts upon the ice a pressure less than atmospheric; and as the remote sides of the

<sup>1</sup> Professor Thomson draws these inferences from the following principle, which appears axiomatic:—If any substance or system of substances be in a condition in which it is free to change its state [as ice, for example, in contact with water at 0° C., is free to melt], and if mechanical forces be applied to it in such a way that the occurrence of the change of state will make it lose the potential energy due to these forces without receiving other potential energy as an equivalent; then the substance or system will pass into the changed state.

blocks are exposed to atmospheric pressure, there is a resultant force urging them together and producing stress at the small surface of contact. Melting of the ice therefore occurs at the places of contact, and the cold thus evolved freezes the adjacent portions of the water film, which, being at less than atmospheric pressure, will begin to freeze at a temperature a little above the ordinary freezing-point.

As regards the amount of the force urging the pieces together, if two flat pieces of ice be supported with their faces vertical, and if they be united by a film from whose lower edge water trickles away, the hydrostatic pressure at any point within this film is less than atmospheric by an amount represented, in weight of water, by the height of this point above the part from which water trickles. If, for simplicity, we suppose the film circular, the plates will be pressed together with a force equal to the weight of a cylinder of water whose base is the film and whose height is the radius.

**90. Apparent Plasticity of Ice. Motion of Glaciers.**—A glacier may be described in general terms as a mass of ice deriving its origin from mountain snows, and extending from the snow-fields along channels in the mountain sides to the valleys beneath.

The first accurate observations on the movements of glaciers were made in 1842, by the late Professor (afterwards Principal) J. D. Forbes, who established the fact that glaciers descend along their beds with a motion resembling that of a pailful of mortar poured into a sloping trough; the surface moving faster than the bottom and the centre faster than the sides. The chief motion occurs in summer. He summed up his view by saying, "A glacier is an imperfect fluid, or a viscous body which is urged down slopes of a certain inclination by the mutual pressure of its parts."

This apparent viscosity is explained by the principles of § 87. According to these principles the ice should melt away at the places where stress is most severe, an equivalent quantity of ice being formed elsewhere. The ice would thus gradually yield to the applied forces, and might be moulded into new forms, without undergoing rupture. Breaches of continuity might be produced in places where the stress consisted mainly of a pull, for the pull would lower the freezing-point, and thus indirectly as well as directly tend to produce ruptures, in the form of fissures transverse to the direction of most intense pull. The effect of compression in any direction would, on the other hand, be, not to crack the ice, but to melt a portion of its interior sufficient to relieve the pressure in the particular part affected,

and to transfer the excess of material to neighbouring parts, which must in their turn give way in the same gradual manner.

In connection with this explanation it is to be observed that the temperature of a glacier is always about  $0^{\circ}$  C., and that its structure is eminently porous and permeated with ice-cold water. These are conditions eminently favourable (the former, but not the latter, being essential) to the production of changes of form depending on the lowering of the melting-point by stresses.

This explanation is due to Professor J. Thomson<sup>1</sup> (*British Association Report*, 1857). Professor Tyndall had previously attempted to account for the phenomena of glacier motion by supposing that the ice is fractured by the forces to which it is subjected, and that the broken pieces, after being pushed into their new positions, are united by regelation. In support of this view he performed several very interesting and novel experiments on the moulding of ice by pres-

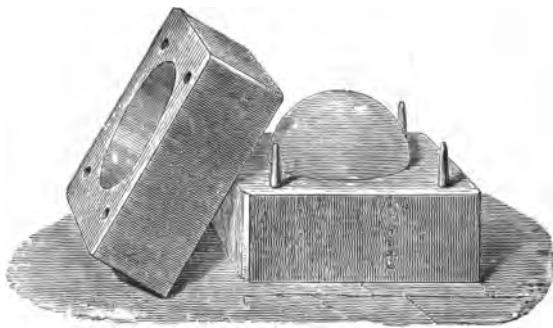


Fig. 53.—Ice Moulded by Pressure.

sure, such as striking medals of ice with a die, and producing a clear transparent cake of ice by powerfully compressing broken pieces in a boxwood mould (Fig. 53).

Interesting experiments on the plasticity of ice may be performed by filling an iron shell with water and placing it in a freezing-mixture, leaving the aperture open. As the water freezes, a cylinder of ice will be gradually protruded. This experiment is due to Mr.

<sup>1</sup> If it should be objected that the lowering of the melting-point by stress is too insignificant to produce the vast effects here attributed to it, the answer is that, when ice and water are present together, the slightest difference is sufficient to determine which portion of the water shall freeze, or which portion of the ice shall melt. In default of a more powerful cause, those portions of ice which are most stressed will melt first.

Christie. Principal Forbes obtained a similar result by using a very strong glass jar; and by smearing the interior, just below the neck, with colouring matter, he demonstrated that the external layer of ice which was first formed, slid along the glass as the freezing proceeded, until it was at length protruded beyond the mouth.

In the experiments of Major Williams, described in § 85, it is probable that much of the water remained unfrozen until its pressure was relieved by the bursting of the shells.

## CHAPTER VIII.

### EVAPORATION AND CONDENSATION.

**91. Transformation into the State of Vapour.**—The majority of liquids, when left to themselves in contact with the atmosphere, gradually pass into the state of vapour and disappear. This phenomenon occurs much more rapidly with some liquids than with others, and those which evaporate most readily are said to be the most volatile. Thus, if a drop of ether be let fall upon any substance, it disappears almost instantaneously; alcohol also evaporates very quickly, but water requires a much longer time for a similar transformation. The change is in all cases accelerated by an increase of temperature; in fact, when we *dry* a body before the fire, we are simply availing ourselves of this property of heat to hasten the evaporation of the moisture of the body. Evaporation may also take place from solids. Thus camphor, iodine, and several other substances pass directly from the solid to the gaseous state, and we shall see hereafter that the vapour of ice can be detected at temperatures far below the freezing-point.

Evaporation, unlike fusion, occurs over a very wide range of temperature. There appears, however, to be a temperature for each substance, below which evaporation, if it exist at all, is insensible to ordinary tests. This is the case with mercury at 0° C., and with sulphuric acid at ordinary atmospheric temperatures.

**92. Vapour, Gas.**—The words *gas* and *vapour* have no essential difference of meaning. A vapour is the gas into which a liquid is changed by evaporation. Every gas is probably the vapour of a liquid. The word *vapour* is especially applied to the gaseous condition of bodies which are usually met with in the liquid or solid state, as water, sulphur, &c.; while the word *gas* generally denotes a

body which, under ordinary conditions, is never found in any state but the gaseous.

**93. Pressure of Vapours. Maximum Pressure and Density.**—The characteristic property of gases is the elastic force<sup>1</sup> with which they tend to expand. This may be exemplified in the case of vapours by the following experiment.

A glass globe A (Fig. 54) is fitted with a metal cap provided with two openings, one of which can be made to communicate with a mercurial manometer, while the other is furnished with a stop-cock R. The globe is first exhausted of air by establishing communication through R with an air-pump. The mercury rises in the left-hand and falls in the right-hand branch of the manometer; the final difference of level in the two branches differing from the height of the barometer only by the very small quantity representing the pressure of the air left behind by the machine. The stop-cock R is then closed, and a second stop-cock R' surmounted by a funnel is fixed above it. The hole in this second stop-cock, instead of going quite through the metal, extends only half-way; so as merely to form a cavity. This cavity serves to introduce a liquid into the globe, without any communication taking place between the globe and the external air. For this purpose we have only to fill the funnel with a liquid, to open the cock R, and to turn that at R' backwards and forwards several times. It will be found that after the introduction of a small quantity of liquid into the globe, the mercurial column begins to descend in the left branch of the manometer, thus indicating an increase of elastic force. This elastic force goes on increasing as a greater quantity of liquid is introduced into the globe; and as no liquid is visible in the globe, we must infer that it evaporates as fast as it is introduced, and that the fall of the mercurial column is caused by the elastic force of the vapour thus formed.

This increase of pressure, however, does not go on indefinitely. After a time the difference of level in the two branches of the manometer ceases to increase, and a little of the unevaporated liquid may be seen in the globe, which increases in quantity as more liquid is

<sup>1</sup> The terms "pressure," "tension," and "elastic force" are often used interchangeably to denote the stress existing in a vapour or gas. "Tension" is the ordinary term employed in this sense in French books. The best English authorities upon elasticity, however, employ the two terms "pressure" and "tension" to denote two opposite things; a pressure is a push, and a tension is a pull. Gases and vapours cannot pull, they can only push, and they are constantly pushing in all directions; hence they are never in a state of *tension*, but are always in a state of *pressure*.

introduced. From this important experiment we conclude that there is a limit to the quantity of vapour which can be formed at a given temperature in an empty space. When this limit is reached, the space is said to be *saturated*, and the vapour then contained in it is at *maximum pressure*, and at *maximum density*. It evidently fol-

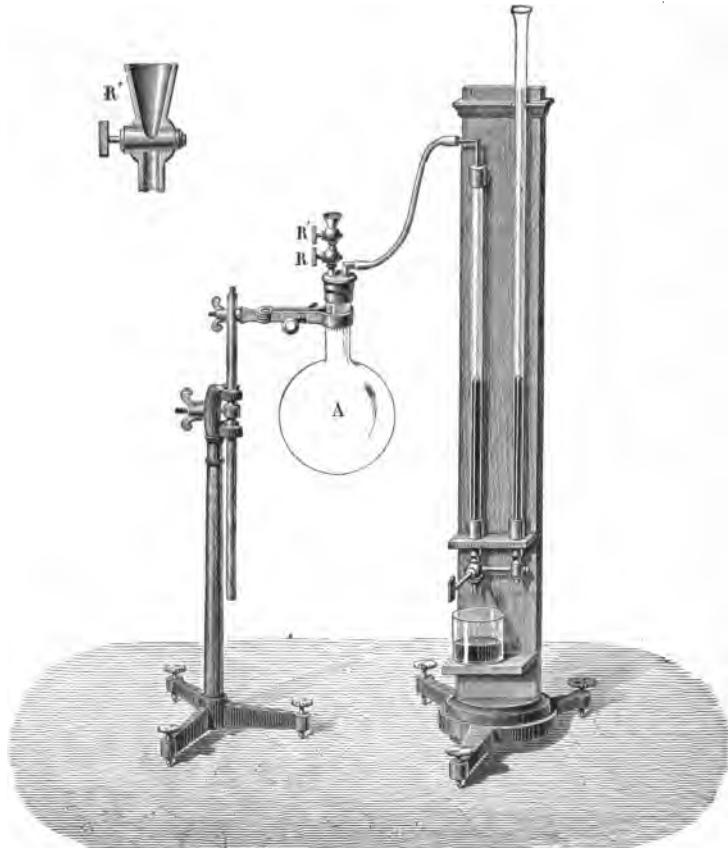


Fig. 54.—Apparatus for studying the Formation of Vapours.

lows from this that if a quantity of vapour at less than its maximum density be inclosed in a given space, and then compressed at constant temperature, its pressure and density will increase at first, but that after a time a point will be reached when further compression, instead of increasing the density and pressure of the vapour, will only cause some of it to pass into the liquid state. This last result may be directly verified by the following experiment. A barometric tube

*a b* (Fig. 55) is filled with mercury, with the exception of a small space, into which a few drops of ether are introduced, care having first been taken to expel any bubbles of air which may have remained

adhering to the mercury. The tube is then inverted in the deep bowl *MN*, when the ether ascends to the surface of the mercury, is there converted into vapour, and produces a sensible depression of the mercurial column. If the quantity of ether be sufficiently small, and if the tube be kept sufficiently high, no liquid will be perceived in the space above the mercury; this space, in fact, is not saturated. The pressure of the vapour which occupies it is given by the difference between the height of the column in the tube and of a barometer placed beside it. If the tube be gradually lowered, this difference will at first be seen to increase, that is, the pressure of the vapour of ether increases; but if we continue the process, a portion of liquid ether will be observed to collect above the mercury, and after this, if we lower the tube any further, the height of the mercury in it remains invariable. The only effect is to increase the quantity of liquid deposited from the vapour.<sup>1</sup>



Fig. 55.—Maximum Tension of Vapours.

globe, and let the globe be subjected to an increase of temperature. An increase of elastic force will at once be indicated by the manometer, while the quantity of liquid will be diminished. The maximum pressure of a vapour, therefore, and also its maximum density, increase with the temperature; and consequently, in order to saturate

<sup>1</sup> Strictly speaking, there will be a slight additional depression of the mercurial column due to the weight of the liquid thus deposited on its summit; but this effect will generally be very small, owing to the smallness of the quantity of liquid.

a given space, a quantity of vapour is required which increases with the temperature.

Vapour which is at less than the maximum density is called *superheated vapour*; because it can be obtained by giving heat to vapour at maximum density at a lower temperature.

Fig. 56 is a graphical representation of the rate at which the maximum density of aqueous vapour increases with the temperature from  $-20^{\circ}$  to  $+35^{\circ}$  C. Lengths are laid off on the base-line AB, to represent temperatures, and ordinates are erected at every fifth de-

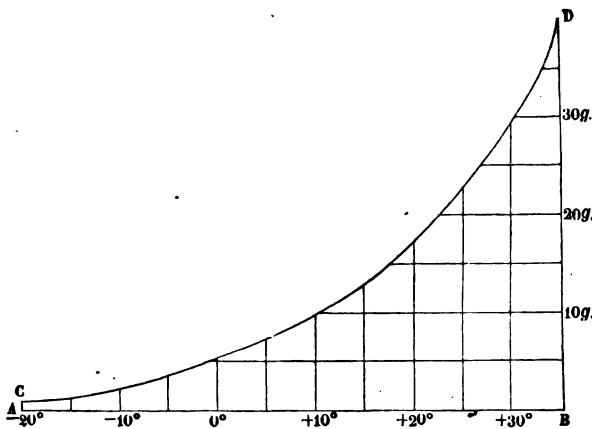


Fig. 56.—Saturation at different Temperatures.

gree, proportional to the masses of vapour required to saturate the same space at different temperatures. The curve CD, drawn through the extremities of these ordinates, is the curve of vapour-density as a function of temperature. The figures on the right hand indicate the number of grammes of vapour required to saturate a cubic metre.

**95. Mixture of Gas and Vapour.** Dalton's Laws.—The experiments with the apparatus of Fig. 54 may be repeated after filling the globe with dry air, or any other dry gas, and the results finally obtained will be the same as with the exhausted globe. If, as before, we introduce successive small quantities of a liquid, it will be converted into vapour, and the pressure will go on increasing till saturation is attained; the elastic force of vapour will then be found to be exactly the same as in the case of the vacuous globe, and the quantity of liquid evaporated will also be the same.

There is, however, one important difference. In the vacuum the complete evaporation of the liquid is almost instantaneous; in a gas,

on the other hand, the evaporation and consequent increase of pressure proceed with comparative slowness; and the difference between the two cases is more marked in proportion as the pressure of the gas is greater.

We may lay down, then, the two following laws (called, from their discoverer, Dalton's laws) for the mixture of a vapour with a gas:—

1. *The mass of vapour which can be contained in a given space is the same whether this space be empty or filled with gas.*

2. *When a gas is saturated with vapour, the actual pressure of the mixture is the sum of the pressures due to the gas and vapour separately; that is to say, it is equal to the pressure which the gas would exert if it alone occupied the whole space, plus the maximum pressure of vapour for the temperature of the mixture.*

This second law comes under the general rule for determining the pressure of a mixture of gases (see Part I.); and the rule still applies to a mixture of gas and vapour when the quantity of the latter falls short of saturation. Each element in a mixture of gases and vapours exerts the same pressure on the walls of the containing vessel as it would exert if the other elements were removed.

It is doubtful, however, whether these laws are rigorously true. It would rather appear from some of Regnault's experiments, that the quantity of vapour taken up in a given space is slightly, though almost insensibly, diminished, as the density of the gas which occupies the space is increased.

96. **Liquefaction of Gases.**—When vapour exists in the state of saturation, any diminution in the volume must, if the temperature is preserved constant, involve the liquefaction of as much of the vapour as would occupy the difference of volumes; and the vapour which remains will still be at the original density and tension. A vapour existing by itself may therefore be completely liquefied by subjecting it to a pressure exceeding, by ever so slight an amount, the maximum tension corresponding to the temperature, provided that the containing vessel is prevented from rising in temperature.

Again, if a vapour at saturation be subjected to a fall of temperature, while its volume remains unchanged, a portion of it must be liquefied corresponding to the difference between the density of saturation at the higher and at the lower temperature. This operation will obviously diminish the pressure, since this will now be the maximum pressure corresponding to the lower instead of to the higher temperature.

There are therefore two distinct means of liquefying a vapour—increase of pressure, and lowering of temperature. They are employed sometimes separately, and sometimes in conjunction.

Fig. 57 represents the apparatus usually employed for obtaining sulphurous acid in the liquid state. The gas, which is generated in a glass globe, passes first into a washing-bottle, then through a drying-tube, and finally into a tube surrounded with a freezing-mixture of snow and salt.

Pouillet's apparatus for showing the unequal compressibilities of different gases (see Part I.) serves to liquefy most gases by means of compression. In order to ascertain the pressures at which liquefaction takes place, or, in other words, the maximum pressures of gases, one of the tubes in that apparatus is replaced by a shorter tube, containing air, and serving as a manometer.

By this means Pouillet found that, at the temperature of  $10^{\circ}$  C., sulphurous acid is liquefied by a pressure of  $2\frac{1}{2}$  atmospheres, nitrous oxide by a pressure of 43, and carbonic acid by a pressure of 45 atmospheres.

**97. Faraday's Method.**—Faraday, who was the first to conduct methodical experiments on the liquefaction of gases, employed, in the first instance, the simple apparatus represented in Fig. 58. It con-

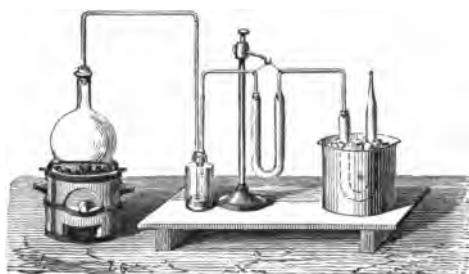


Fig. 57.—Liquefaction of Sulphurous Acid.

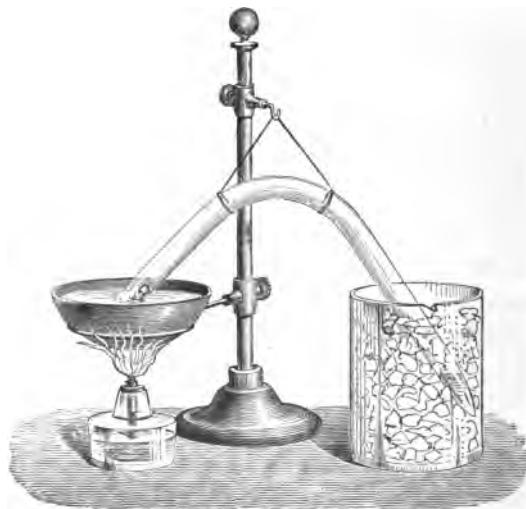


Fig. 58.—Faraday's Apparatus.

sists of a very strong bent glass tube, one end of which contains ingredients which evolve the gas on the application of heat, while the other is immersed in a freezing-mixture. The pressure produced by the evolution of the gas in large quantity in a confined space, combines with the cold of the freezing-mixture to produce liquefaction of the gas, and the liquid accordingly collects in the cold end of the tube.

Thilorier, about the year 1834, invented the apparatus represented in Fig. 59, which is based on this method of Faraday, and is intended for liquefying carbonic acid gas. This operation requires the enormous pressure of about fifty atmospheres at ordinary temperatures. If a slight rise of temperature occur from the chemical actions attending the production of the gas, a pressure of 75 or 80 atmospheres may not improbably be required. Hence great care is necessary in testing the strength of the metal employed in the construction of the apparatus. It was formerly made of cast-iron, and strengthened by wrought-iron hoops; but the construction has since been changed on account of a terrible explosion, which cost the life of one of the operators. At present the vessels are formed of three parts; the inner one of lead, the next *e*, which completely envelops this, of copper, and finally, the hoops *ff* of wrought iron (Fig. 59), which bind the whole together. The apparatus consists of two distinct reservoirs. In the generator C is placed bicarbonate of soda, and a vertical tube *a*, open at top, containing sulphuric acid. By imparting an oscillatory movement to the vessel about the two pivots which support it near the middle, the sulphuric acid is gradually discharged, and the carbonic acid is evolved, and becomes liquid in the interior. The generator is then connected with the condenser C' by the tube *t*, and the stop-cocks R and R' are opened. As soon as the two vessels are in communication, the liquid carbonic acid passes into the condenser, which is at a lower temperature than the generator, and represents the cold branch of Faraday's apparatus. The generator can then be disconnected and recharged, and thus several pints of liquid carbonic acid may be obtained.

In the foregoing methods, the pressure which produces liquefaction is furnished by the evolution of the gas itself.

In some other forms of apparatus the pressure is obtained by the use of one or more compression-pumps, which force the gas from the vessel in which it is generated into a second vessel, which is kept cool either by ice or a freezing-mixture. The apparatus of this kind

which is most extensively used is that devised by Bianchi. It consists of a compression-pump driven by a crank furnished with a fly-wheel, and turned by hand.

Faraday, in his later experiments, employed two pumps, the first

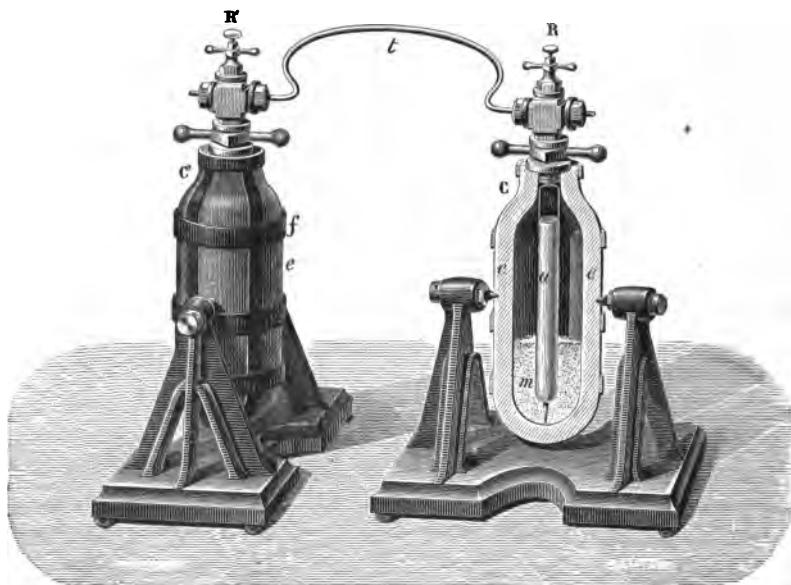


Fig. 59.—Thilorier's Apparatus.

having a piston of an inch, and the second of only half an inch diameter. The first pump in the earlier stage of the operation forced the gas through the second into the receiver. In the later stage the second pump was also worked, so as to force the gas already condensed to 10, 15, or 20 atmospheres into the receiver at a much higher pressure. The receiver was a tube of green bottle-glass, and was immersed in a very intense freezing-mixture, consisting of solid carbonic acid and ether, the cooling effect being sometimes increased by exhausting the air and vapour from the vessel containing the freezing-mixture, so as to promote more rapid evaporation.

**98. Latent Heat of Vaporization. Cold produced by Evaporation.**—The passage from the liquid to the gaseous state is accompanied by the disappearance of a large quantity of heat. Whenever a liquid evaporates without the application of heat, a depression of temperature occurs. Thus, for instance, if any portion of the skin be kept moist with alcohol or ether, a decided sensation of cold is felt. Water

produces the same effect in a smaller degree, because it evaporates less rapidly.

The heat which thus disappears in virtue of the passage of a liquid into the gaseous condition, is called the *latent heat of vaporization*. Its amount varies according to the temperature at which the change is effected, and it is exactly restored when the vapour returns to the liquid form, provided that both changes have been effected at the same temperature. Its amount for vapour of water at the temperature  $100^{\circ}$  C. is  $536^{\circ}$ ; that is to say, the quantity of heat which disappears in the evaporation of a pound of water at this temperature, and which reappears in the condensation of a pound of steam at the same temperature, would be sufficient to raise the temperature of 536 pounds of water from  $0^{\circ}$  to  $1^{\circ}$ .

The latent heat of vaporization plays an important part in the heating of buildings by steam. A pound of steam at  $100^{\circ}$ , in becoming reduced to water at  $30^{\circ}$ , gives out as much heat as about  $8\frac{2}{3}$  lbs. of water at  $100^{\circ}$  in cooling down to the same temperature.

**99. Leslie's Experiment.**—Water can be easily frozen by the cold resulting from its own evaporation, as was first shown by Leslie in a celebrated experiment. A small capsule (Fig. 60) of copper is taken, containing a little water, and is placed above a vessel containing strong sulphuric acid. The whole is placed under the receiver of an air-pump, which is then exhausted. The water evaporates with great rapidity, the vapour being absorbed by the sulphuric acid as fast as it is formed, and ice soon begins to appear on the surface. The experiment is, however, rather difficult to perform successfully. This arises from various causes.

In the first place, the vapour of water which occupies the upper part of the receiver is only imperfectly absorbed; and, in the second place, as the upper layer of the acid becomes diluted by absorbing the vapour, its affinity for water rapidly diminishes.

These obstacles have been removed by an apparatus invented by M. Carré, which enables us to obtain a considerable mass of ice in a few minutes. It consists (Fig. 61) of a leaden reservoir containing



Fig. 60.—Leslie's Experiment.

sulphuric acid. At one extremity is a vertical tube, the end of which is bent over and connected with a flask containing water. The other extremity of the reservoir communicates with an air-pump, to the

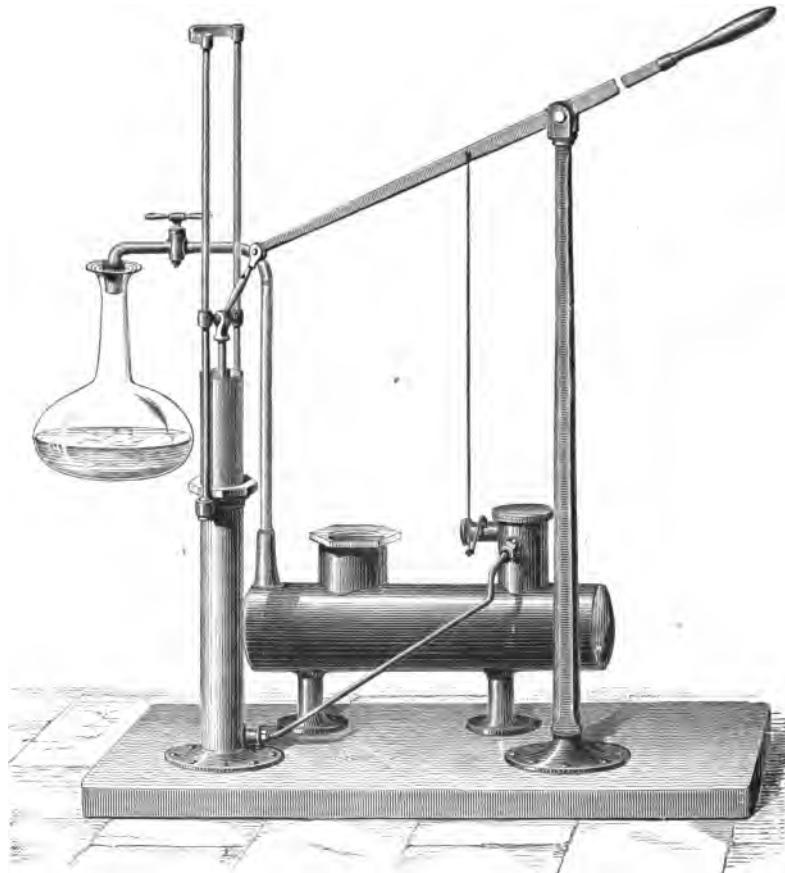


Fig. 61.—Carré's Apparatus for freezing by Sulphuric Acid.

handle of which is fitted a metallic rod, which drives an agitator immersed in the acid. By this means the surface of the acid is continually renewed, absorption takes place with regularity, and the water is rapidly frozen.

**100. Cryophorus.**—Wollaston's cryophorus (Fig. 62) consists of a bent tube with a bulb at each end. It is partly filled with water, and hermetically sealed while the liquid is in ebullition, thus expelling the air.

When an experiment is to be made, all the liquid is passed into the bulb B, and the bulb A is plunged into a freezing-mixture, or into pounded ice. The cold condenses the vapour in A, and thus produces rapid evaporation of the water in B. In a short time needles of ice appear on the surface of the liquid.

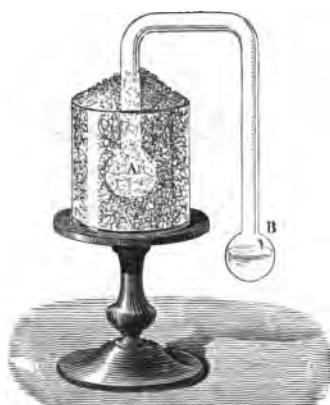


Fig. 62.—Oryphorus.

**101. Freezing of Water by the Evaporation of Ether.**—Water is poured into a glass tube dipped into ether, which is contained in a glass vessel for the purpose (Fig. 63). By means of a pair of bellows a current of air is made to pass through the ether; evaporation is quickly produced, and at the end of a few minutes the water in the tube is frozen.

If, instead of promoting evaporation of the ether by means of a



Fig. 63.—Freezing of Water by Evaporation of Ether.

current of air, the vessel were placed under the exhausted receiver of an air-pump, a much greater fall of temperature would be ob-

tained, and even mercury might easily be frozen. This experiment, however, is injurious to the pump, owing to the solvent action of the ether on the oil with which the valves and other moving parts are lubricated.

**102. Freezing of Mercury by means of Sulphurous Acid.**—Mercury may be frozen by means of liquid sulphurous acid, which is much more volatile than ether. In order to escape the suffocating action of the gas, the experiment is performed in the following manner:—

Into a glass vessel (Fig. 64) are poured successively mercury and liquid sulphurous acid. The vessel is closed by an india-rubber stopper, in which two glass tubes are fitted. One of these dips to the bottom of the sulphurous acid, and is connected at its outer end with a bladder full of air. Air is passed through the liquid by compressing the bladder, and escapes, charged with vapour, through the second opening, which is fitted with an india-rubber tube leading to the open air. Evaporation proceeds with great rapidity, and the mercury soon freezes.



Fig. 64.  
Freezing of Mercury  
by Evaporation of  
Sulphurous Acid.

**103. Carré's Ammoniacal Apparatus.**—The apparatus invented some years ago by M. Carré for making ice is another instance of the ap-

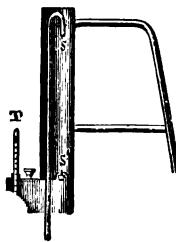


Fig. 65.

Carré's Apparatus for Freezing by Ammonia.

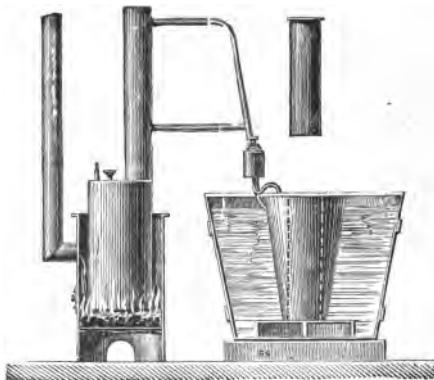


Fig. 66.

plication of cold produced by evaporation. It consists (Figs. 65 and 66) of two parts, a boiler and a cooler. The boiler is of wrought iron, and is so constructed as to give a very large heating surface. It is three-quarters filled with a saturated solution of ammonia.

which contains from six to seven hundred times its volume of gas. The cooler is of an annular form, and in the central space is placed a vessel containing the water to be frozen. In the sides of the cooler are a number of small cells, the object of which is to increase its surface of contact with the water in which it is immersed.

In the first part of the experiment, which is represented in the figure, the boiler is placed upon a fire, and the temperature raised to  $130^{\circ}$ , while the cooler is surrounded with cold water. Ammoniacal gas is given off, passes into the cooler by the valve *s* opening upwards, and is condensed in the numerous cells above mentioned. This first part of the operation, in the small machines for domestic use, occupies about three-quarters of an hour. In the second part of the operation, the cylindrical vessel containing the water to be frozen is placed in the central space; the cooler is surrounded with an envelope of felt, which is a very bad conductor of heat, and the boiler is immersed in cold water. The water in the boiler, as it cools, is able again to receive and dissolve the gas, which enters by the valve *s* of the bent siphon-shaped tube. The liquid ammonia in the cooler accordingly evaporates with great rapidity, producing a fall of temperature which freezes the water in the inclosed vessel.

**104. Solidification of Carbonic Acid.**—When a small orifice is opened in a vessel containing liquid carbonic acid, evaporation proceeds so rapidly that the cold resulting from it freezes a portion of the vapour, which takes the form of fine snow, and may be collected in considerable quantity.

This carbonic acid snow, which was first obtained by Thilorier, is readily dissolved by ether, and forms with it one of the most intense freezing-mixtures known. By immersing tubes containing liquefied gases in this mixture, Faraday succeeded in reducing several of them, including carbonic acid, cyanogen, and nitrous oxide, to the form of clear transparent ice, the fall of temperature being aided, in some of his experiments, by employing an air-pump to promote more rapid evaporation of carbonic acid from the mixture. By the latter process he was enabled to obtain a temperature of  $-166^{\circ}$  F. ( $-110^{\circ}$  C.) as indicated by an alcohol thermometer, the alcohol itself being reduced to the consistence of oil. Despretz, by means of the cold produced by a mixture of solid carbonic acid, liquid nitrous oxide, and ether, rendered alcohol so viscid that it did not run out when the vessel which contained it was inverted.

**105. Continuity of the Liquid and Gaseous States. Critical Tem-**

perature.—Remarkable results were obtained by Cagniard de la Tour<sup>1</sup> by heating volatile liquids (alcohol, petroleum, and sulphuric ether) in closed tubes of great strength, and of capacity about double the volume of the inclosed liquid. At certain temperatures (36° C. for alcohol, and 42° for ether) the liquid suddenly disappeared, becoming apparently converted into vapour.

Drion,<sup>2</sup> by similar experiments upon hydrochloric ether, hyponitric acid, and sulphurous acid, showed—

1. That the coefficients of apparent expansion of these liquids increase rapidly with the temperature.

2. That they become equal to the coefficient of expansion of air, at temperatures much lower than those at which total conversion into vapour occurs.

3. That they may even become double and more than double the coefficient of expansion of air; for example, at 130° C. the coefficient of expansion of sulphurous acid was .009571.

Thilorier had previously shown that the expansion of liquid carbonic acid between the temperatures 0° and 30° C. is four times as great as that of air.

Drion further observed, that when the temperature was raised very gradually to the point of total vaporization, the free surface lost its definition, and was replaced by a nebulous zone without definite edges and destitute of reflecting power. This zone increased in size both upwards and downwards, but at the same time became less visible, until the tube appeared completely empty. The same appearances were reproduced in inverse order on gradually cooling the tube.

When the liquid was contained in a capillary tube, or when a capillary tube was partly immersed in it, the curvature of the meniscus and the capillary elevation decreased as the temperature rose, until at length, just before the occurrence of total vaporization, the surface became plane, and the level was the same within as without the tube.

Dr. Andrews, by a series of elaborate experiments on carbonic acid, with the aid of an apparatus which permitted the pressure and temperature to be altered independently of each other, showed that at temperatures above 31° C. this gas cannot be liquefied, but, when subjected to intense pressure, becomes reduced to a condition

<sup>1</sup> *Ann. de Chim.* II. xxi

<sup>2</sup> *Ann. de Chim.* III. lvi.

in which, though homogeneous, it is neither a liquid nor a gas. When in this condition, lowering of temperature under constant pressure will reduce it to a liquid, and diminution of pressure at constant temperature will reduce it to a gas; but in neither case can any breach of continuity be detected in the transition.

On the other hand, at temperatures below 31°, the substance remains completely gaseous until the pressure reaches a certain limit depending on the temperature, and any pressure exceeding this limit causes liquefaction to commence and to continue till the whole of the gas is liquefied, the boundary between the liquefied and unliquefied portions being always sharply defined.

The temperature 31° C., or more exactly 30.92° C. (87.7° F.), may therefore be called the *critical temperature* for carbonic acid; and it is probable that every other substance, whether usually occurring in the gaseous or in the liquid form, has in like manner its own critical temperature. Dr. Andrews found that nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited critical temperatures, which, in the case of some of these substances, were above 100° C.

It is probable that, in the experiments of Cagniard de la Tour and Drion, the so-called total conversion into vapour was really conversion into the intermediate condition.

The continuous conversion of a gas into a liquid may be effected by first compressing it at a temperature above its critical temperature, until it is reduced to the volume which it will occupy when liquefied, and then cooling it below the critical point.

The continuous conversion of a liquid into a gas may be obtained by first raising it above the critical temperature while kept under pressure sufficient to prevent ebullition, and afterwards allowing it to expand.

When a substance is a little above its critical temperature, and occupies a volume which would, at a lower temperature, be compatible with partial liquefaction, very great changes of volume are produced by very slight changes of pressure.

On the other hand, when a substance is at a temperature a little below its critical point, and is partially liquefied, a slight increase of temperature leads to a gradual obliteration of the surface of demarcation between the liquid and the gas; and when the whole has thus been reduced to a homogeneous fluid, it can be made to exhibit an appearance of moving or flickering strife throughout its entire mass

by slightly lowering the temperature, or suddenly diminishing the pressure.

The apparatus employed in these remarkable experiments, which are described in the Bakerian Lecture (*Phil. Trans.* 1869), is shown in Fig. 67, where *cc* are two capillary glass tubes of great strength, one of them containing the carbonic acid or other gas to be experimented on, the other containing air to serve as a manometer. These are connected with strong copper tubes *dd*, of larger diameter, containing water, and communicating with each other through *ab*, the water being separated from the gases by a column of mercury occupying the lower portion of each capillary tube. The steel screws *ss* are the instruments for applying pressure. By screwing either of them forward into the water, the contents of both tubes are compressed, and the only use of having two is to give a wider range of compression. A rectangular brass case (not shown in the figure), closed before and behind with plate-glass, surrounds each capillary tube, and allows it to be maintained at any required temperature by the flow of a stream of water.

**106. Liquefaction and Solidification of Oxygen and Hydrogen.—** Up to quite recent times, air, oxygen, hydrogen, nitrogen, nitric oxide, and marsh-gas had defied all attempts to liquefy them, and were therefore called "permanent gases." But in the latter part of the year 1877 and the beginning of 1878 they were liquefied by two investigators independently.

M. Cailletet, a French engineer, employed an apparatus similar in principle to that of Dr. Andrews described in the preceding section; the gas being compressed in a strong capillary tube by screwing a plunger into water, which transmitted the pressure to mercury in contact with the gas. When the gas had had time to lose its heat of compression, and to attain the low temperature of the inclosure by

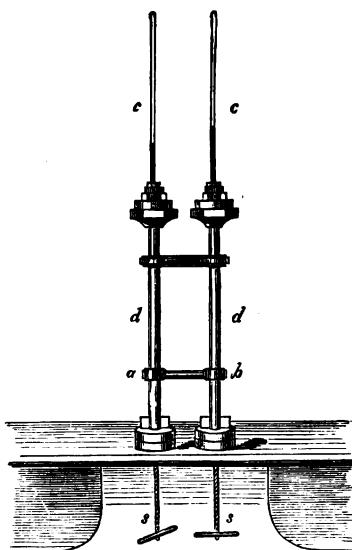


Fig. 67.—Andrews' Apparatus.

which it was surrounded, it was suddenly allowed to expand by unscrewing a second screw plunger provided for the purpose; and under the influence of the intense cold produced by this expansion, the gas in the tube assumed the form of a cloud, showing that drops of liquid were present in it. For thus liquefying oxygen, he employed a pressure of 300 atmospheres, and, before allowing the gas to expand, cooled it to the temperature  $-29^{\circ}$  C. by means of the evaporation of sulphurous acid. For nitrogen he employed a pressure of 200, and for hydrogen of 280 atmospheres.

M. Raoul Pictet, of Geneva, who has devoted much attention to the artificial production of ice, cooled the gas under pressure, by surrounding it with two tubes one within the other, the outer one containing liquid sulphurous acid, which was rapidly evaporated by pumping away its vapour, while the inner one contained solid carbonic acid, which was also evaporated by means of a pump. The temperature of the outer tube was  $-65^{\circ}$  or  $-70^{\circ}$ ; that of the inner about  $-140^{\circ}$ ; and this inner tube immediately surrounded the tube containing the gas which it was desired to liquefy. The pressure was produced, as in Faraday's earlier experiments, by the chemical action which evolved the gas. When time had been given for the compressed gas to take the low temperature of its surroundings, a cock was opened which allowed it to escape through a small orifice into the external air, and the issuing jet was seen to be liquid. In the case of oxygen, the pressure before the escape of the jet was 320 atmospheres, in the case of hydrogen it was 650. The jet of liquid hydrogen was of a steel-blue colour, and after a short time it was changed into a hail of solid particles, showing that hydrogen had not only been liquefied but solidified. In a later experiment the jet of oxygen was submitted to optical tests (by polarized light) which showed that it contained solid particles.

**106A. Dewar's Experiments.** — More recently (1892) Professor Dewar, at the Royal Institution, has liquefied oxygen and some other gases by intense cold at atmospheric pressure. The gas to be liquefied was cooled by the continued evaporation of ethylene and of nitrous oxide, the temperature being sometimes as low as  $-200^{\circ}$  C. Liquid oxygen, in quantities of a pint, was exhibited in an open vessel, its boiling point under atmospheric pressure being  $-180^{\circ}$  C., and its latent heat of evaporation  $80^{\circ}$  C. After filtration it was a clear transparent liquid with a slight blueish tinge.

It was found to be a non-conductor of electricity, and to be so

strongly magnetic that, when placed in the spheroidal state in a cup of rock-salt beneath the poles of an electro-magnet, it leaped up as soon as the magnetizing current was turned on, and formed a bridge of hour-glass shape between the poles, as shown in Fig. 67A.<sup>1</sup> At

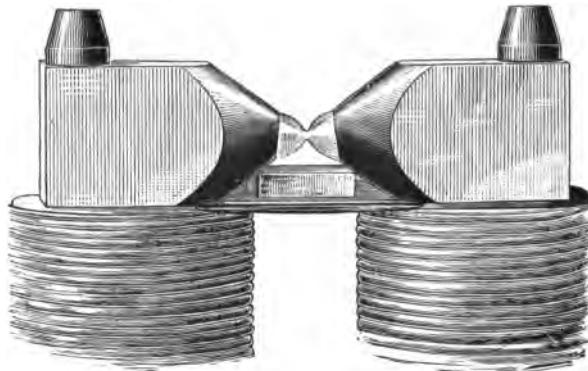


Fig. 67A.—Dewar's Experiment.

the temperature  $-200^{\circ}$  C., it was chemically inert, exhibiting no action on phosphorus or potassium dropped into it.

Air was liquefied in a similar manner, its two constituents going down together into one liquid; and when tested by the electro-magnet all the liquid went to the poles. When it was allowed to evaporate, its nitrogen boiled off before its oxygen. When surrounded by a jacket of liquid oxygen, and subjected to rapid and sustained evaporation of its nitrogen by means of a powerful pump, it was reduced to a solid block of transparent ice. The boiling point of liquid nitrogen was found to be  $-190^{\circ}$  C.

<sup>1</sup> For this figure, which is copied from a photograph, we are indebted to Professor Dewar and the publishers of the *Engineer*.

## CHAPTER IX.

### EBULLITION.

**107. Ebullition.**—When an open vessel containing a liquid is placed upon a fire or held over the flame of a lamp, evaporation at first goes on quietly and the liquid steadily rises in temperature; but after a time the liquid becomes agitated, gives off vapour much faster, and remains nearly constant in temperature. The liquid is now said to *boil* or to be in a state of *ebullition*.

If we observe the gradual progress of the phenomena—as we can easily do in a glass vessel containing water, we shall perceive that, after a time, very minute bubbles are given off; these are bubbles of dissolved air. Soon after, at the bottom of the vessel, and at those parts of the sides which are most immediately exposed to the action of the fire, larger bubbles of vapour are formed, which decrease in volume as they ascend, and disappear before reaching the surface. This stage is accompanied by a peculiar sound, indicative of approaching ebullition, and the liquid is said to be *singing*. The sound is probably caused by the collapsing of the bubbles as they are condensed by the colder water through which they pass. Finally, the bubbles increase in number, growing larger as they ascend, until they burst at the surface, which is thus kept in a state of agitation; and the liquid boils.

**108. Laws of Ebullition.**—The following are the ordinary laws of ebullition.



Fig. 68.—Ebullition.

1. *At the ordinary pressure, ebullition commences at a temperature which is definite for each liquid.*

This law is analogous to that of fusion (§ 72). It follows from this that the boiling-point of any liquid is a *specific* element, serving to determine its nature.

The following table gives the boiling-points of several liquids at the pressure of 760 millimetres:—

Sulphurous acid,	— 10° C.	Spirits of turpentine,	+ 130° C.
Hydrochloric ether,	+ 11°	Phosphorus,	290°
Common ether,	37°	Concentrated sulphuric acid,	325°
Alcohol,	79°	Mercury,	353°
Distilled water,	100°	Sulphur,	440°

2. *The temperature remains constant during ebullition.* If a thermometer be introduced into the glass vessel of Fig. 68, the temperature will be observed to rise gradually during the different stages preceding ebullition; but, when active ebullition has once commenced, no further advance of temperature will be observed.

This phenomenon points to the same conclusion as the cold produced by evaporation. Since, notwithstanding the continuous action of the fire, the temperature remains constant, the conclusion is inevitable, that all the heat produced is employed in doing the work necessary to change the liquid into vapour. The constancy of temperature during ebullition explains the fact that vessels of pewter, tin, or any other easily fusible metal, may be safely exposed to the action of even a very hot fire, provided that they contain water, since the liquid remains at a temperature of about 100°, and its contact prevents the vessel from over-heating. We shall see hereafter that, under certain circumstances, the commencement of ebullition is delayed till the liquid has risen considerably above the permanent temperature which it retains when boiling. The second law also is not absolutely exact. Small fluctuations of temperature occur, and some parts of the liquid are slightly hotter than others. The temperature of the vapour is more constant than that of the water, and is accordingly employed in determining the “fixed points” of thermometers.

3. *The pressure of the vapour given off during ebullition is equal to that of the external air.*

Previous to ebullition, the upper part of the vessel in Fig. 68 contains a mixture of air and vapour, the joint pressure being sensibly equal to that of the external air; but when active ebullition

occurs, the air is expelled, and the upper part of the vessel, from the liquid to the mouth, is occupied by vapour alone, which, being in free communication with the external air, must be sensibly equal to it in pressure.

The following experiment furnishes an interesting confirmation of this third law.

We take a bent tube A, open at the longer extremity, and closed at the shorter. The short branch is filled with mercury, all but a small space containing water; in the long branch the mercury stands a little higher than the bend. Water is now boiled in a glass vessel, and, during ebullition, the bent tube is plunged into the steam. The water occupying the upper part of the short branch is partially converted into steam, the mercury falls, and it *assumes the same level in both branches*. Thus the pressure exerted by the atmosphere at the open extremity of the tube is exactly equal to that exerted by the vapour of water at the temperature of ebullition.

**109. Definition of Ebullition.**—This latter circumstance supplies the true physical definition of ebullition. *A liquid is in ebullition when it gives off vapour of the same pressure as the atmosphere above it.*

The necessity of this equality of tension is easily explained. If a bubble of vapour exists in the interior of a liquid (as at *m*, Fig. 70), it is subject to a pressure exceeding atmospheric by the weight of the liquid above it. As the bubble rises, the latter element of pressure becomes less, and the pressure of the vapour composing the bubble accordingly diminishes, until it is reduced to atmospheric pressure on reaching the surface.

The boiling-point of a liquid at given pressure is therefore neces-



Fig. 69.—Tension of Vapour during Ebullition.

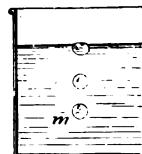


Fig. 70.

sarily fixed, since it is the temperature at which the pressure of the vapour at saturation is equal to this pressure. It must be remarked, however, that the boiling-point varies in the different layers of the liquid, increasing with the depth below the surface. Accordingly, in determining the second fixed point of the thermometer, we have stated that the instrument should be plunged into the steam, and not into the water.

**110. Effect of Pressure upon the Boiling-point.**—It evidently follows from the foregoing considerations that the boiling-point of a liquid must vary with the pressure on the surface; and experiment shows that this is the case. Water, for instance, boils at  $100^{\circ}$  under the external pressure of 760 millimetres; but if the pressure decreases, ebullition occurs at a lower temperature. Under the receiver of an air-pump, water may be made to boil at any temperature between  $0^{\circ}$  and  $100^{\circ}$ . In Carré's apparatus (Fig. 61) the water in the glass bottle is observed to enter into active ebullition a few moments before the appearance of the ice. The reason, therefore, why boiling water has come to be associated in our minds with a fixed temperature is that the variations of atmospheric pressure are comparatively small.

At Paris, for instance, the external pressure varies between 720 and 790 millimetres (28·3 and 31·1 inches), and the boiling-point, in consequence, varies from  $98\cdot5^{\circ}$  to  $101\cdot1^{\circ}$ , the difference being at the rate of about 27<sup>mm</sup> per degree.

**111. Franklin's Experiment.**—The boiling of water at a temperature lower than  $100^{\circ}$  may be shown by the following experiment:—

A little water is boiled in a flask for a sufficient time to expel most of the air contained in it. The flask is then removed from the source of heat, and is at the same time securely corked. To render the exclusion of air still more certain, it may be inverted with the corked end immersed in



Fig. 71.—Franklin's Experiment.

water which has been boiled. Ebullition ceases almost immediately; but if cold water be now poured over the vessel, or, better still, if ice be applied to it, the liquid again begins to boil, and continues to do so for a considerable time. This fact may easily be explained: the contact of the cold water or the ice lowers the temperature and pressure of the steam in the flask, and the decrease of pressure causes the renewal of ebullition.

**112. Determination of Heights by Boiling-point.**—Just as we can determine the boiling-point of water when the external pressure is given, so, if the boiling-point be known, we can determine the external pressure. In either case we have simply to refer to a table of maximum pressures of aqueous vapour at different temperatures.

As the mercurial barometer is essentially unsuitable for portability, Wollaston proposed to substitute the observation of boiling-points as a means of determining pressures. For this purpose he employed a thermometer with a large bulb and with a scale of very long degrees finely subdivided extending only a few degrees above and below 100°. He called this instrument the barometric thermometer.

Regnault has constructed a small instrument for the same purpose, which he calls the *hyprometer*. It consists of a little boiler heated by a spirit-lamp, and terminating in a telescope tube with an opening at the side through which the steam escapes. A thermometer dips into the steam, and projects through the top of the tube so as to allow the temperature of ebullition to be read.

This temperature at once gives the atmospheric pressure by reference to a table of vapour-pressures, and the subsequent computations for determining the height are the same as when the barometer is employed (see Part I.).

When only an approximate result is desired, it may be assumed that the height above sea-level is sensibly proportional to the differ-

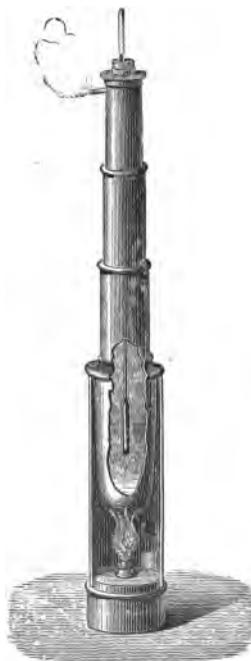


Fig. 72.—Hypsometer.

ence between the observed boiling-point and 100° C., and Soret's formula<sup>1</sup> may be employed, viz.:

$$h = 295 (100 - t),$$

where  $h$  is expressed in metres and  $t$  in degrees Centigrade.

Thus, at Quito, where the boiling-point of water is about 90·1°, the height above sea-level would be  $9\cdot9 \times 295 = 2920$  metres, which agrees nearly with the true height 2808 metres.

At Madrid, at the mean pressure, the boiling-point is 97·8°, which gives  $2\cdot2 \times 295 = 649$  metres; the actual height being 610 metres.

**113. Papin's Digester.**—While a decrease of pressure lowers the boiling-point, an increase of pressure raises it. Accordingly, by putting the boiler in communication with a reservoir containing air at the pressure of several atmospheres, we can raise the boiling-point to

110°, 115°, or 120°; a result often of great utility in the arts. But in order that the liquid may actually enter into ebullition, the space above the liquid must be sufficiently large and cool to allow of the condensation of the steam. In a confined vessel, water may be raised to a higher temperature than would be possible in the open air, but it will not boil. This is the case in the apparatus invented by the celebrated Papin, and called after him *Papin's digester*. It is a bronze vessel of great strength, covered with a lid



Fig. 73.—Papin's Digester.

secured by a powerful screw. It is employed for raising water to very high temperatures, and thus obtaining effects which would not be possible with water at 100°, such, for example, as dissolving the gelatine contained in bones.

It is to be observed that the pressure of the steam increases rapidly

<sup>1</sup> If  $h$  be expressed in feet, and  $t$  in degrees Fahrenheit, the formula becomes

$$h = 538 (212 - t).$$

with the temperature, and may finally acquire an enormous power. Thus, at  $200^{\circ}$ , the pressure is that of 16 atmospheres, or about 240 pounds on the square inch. In order to obviate the risk of explosion, Papin introduced a device for preventing the pressure from exceeding a definite limit. This invention has since been applied to the boilers of steam-engines, and is well known as the *safety-valve*. It consists of an opening, closed by a conical valve or stopper, which is pressed down by a lever loaded with a weight. Suppose the area of the lower end of the stopper to be 1 square inch, and that the pressure is not to exceed 10 atmospheres, corresponding to a temperature of  $180^{\circ}$ . The magnitude and position of the weight are so arranged that the pressure on the hole is 10 times 15 pounds. If the tension of the steam exceed 10 atmospheres, the lever will be raised, the steam will escape, and the pressure will thus be relieved.

It is a remarkable fact that, while the steam from an ordinary kettle scalds the hand, no injury is sustained by holding the hand in the jet of steam which issues from the safety-valve of a high-pressure boiler, although the temperature within the boiler is much higher than that within the kettle. The explanation appears to be that the steam which issues from the safety-valve is dry, and, like any other gas, is slow in raising the temperature of bodies exposed to it; while the steam from the kettle, being at saturation, deposits scalding-hot water on surfaces colder than itself. The subject has been much discussed in connection with "the specific heat of saturated steam" (see § 258). The expansion of the steam in escaping through the safety-valve has a powerful cooling effect, which would of itself be sufficient to produce partial condensation; but this effect is counteracted by the heat generated by the violent friction of the steam against the sides of the orifice, and the resultant effect is to leave the steam in a superheated condition.

**114. Boiling-point of Saline Solutions.**—When water holds saline matters in solution, the boiling-point rises as the proportion of saline matter in the water increases. Thus with sea-salt the boiling-point can be raised from  $100^{\circ}$  to  $108^{\circ}$ .

When the solution is not saturated, the boiling-point is not fixed, but rises gradually as the mixture becomes concentrated; but at a certain stage the salt begins to be precipitated, and the temperature then remains invariable. This is to be considered the normal boiling-point of the saturated solution. Supersaturation, however, sometimes occurs, the temperature gradually rising above the normal boiling-

point without any deposition of the salt, until all at once precipitation begins, and the thermometer falls several degrees.

The steam emitted by saline solutions consists of pure water, and it is frequently asserted to have the same temperature as the steam of pure water boiling under the same pressure; but the experiments of Magnus and others have shown that this is not the case. Magnus, for example,<sup>1</sup> found that when a solution of chloride of calcium was boiling at 107°, a thermometer in the steam indicated 105 $\frac{1}{4}$ °, and when by concentration the boiling-point had risen to 116°, the thermometer in the steam indicated 111.2°.

These and other observations seem to indicate that the steam emitted by a saline solution when boiling, is in the condition in which the steam of pure boiling water would be, if heated, under atmospheric pressure, to the temperature of the boiling solution. It can therefore be cooled down to the boiling-point of pure water without undergoing any liquefaction. When cooled to this point, it becomes saturated,<sup>2</sup> and precisely resembles the steam of pure water boiling under the same pressure. When saturated steam loses heat, it does not cool, but undergoes partial liquefaction, and it does not become completely liquefied till it has lost as much heat as would have cooled more than a thousand times its weight of superheated steam one degree Centigrade.

**115. Boiling-point of Liquid Mixtures.**—A mixture of two liquids which have an attraction for each other, and will dissolve each other freely in all proportions—for example, water and alcohol—has a boiling-point intermediate between those of its constituents. But a mechanical mixture of two liquids between which no solvent action takes place—for example, water and sulphide of carbon—has a boiling-point lower than either of its constituents. If steam of water is passed into liquid sulphide of carbon, or if sulphide of carbon vapour is passed into water, a mixture is obtained which boils at 42.6° C., being four degrees lower than the boiling-point of sulphide of carbon alone. This apparent anomaly is a direct consequence of the laws of vapours stated in § 95; for the boiling-point of such a mixture is the temperature at which the sum of the pressures of the two independent vapours is equal to one atmosphere.

**116. Difficulty of Boiling without Air.**—The presence of air in the

<sup>1</sup> Poggendorff's *Annalen*, cxii. p. 415.

<sup>2</sup> *Saturated steam* is the ordinary designation of steam at the maximum density and pressure for its actual temperature. The term *superheated* has been explained in § 94.

midst of the liquid mass is a necessary condition of regularity of ebullition, and of its production at the normal temperature; this is shown by several convincing experiments.

1. *Donny's Experiment.*—We take a glass tube bent twice, and terminated at one of its extremities by a series of bulbs. The first step is to wash it carefully with alcohol and ether, finally leaving in it some diluted sulphuric acid. These operations are for the purpose of removing the solid particles adhering to the sides, which always detain portions of air. Water is then introduced and boiled long enough to expel the air dissolved in it, and while ebullition is proceeding, the end of the apparatus is hermetically sealed. The other

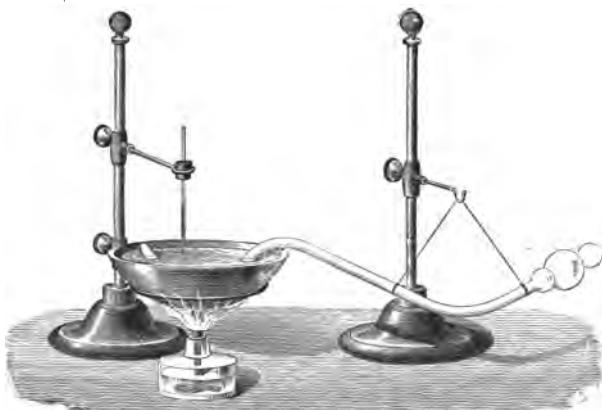


Fig. 74.—*Donny's Experiment.*

extremity is now plunged in a strong solution of chloride of calcium, which has a very high boiling-point, and the tube is so placed that all the water shall lie in this extremity; it will then be found that the temperature may be raised to  $135^{\circ}$  without producing ebullition. At about this temperature bubbles of steam are seen to be formed, and the entire liquid mass is thrown forward with great violence. The bulbs at the end of the tube are intended to diminish the shock thus produced.

2. *Dufour's Experiment.*—This experiment is still more decisive. A mixture of linseed-oil and oil of cloves, whose respective densities are about .93 and 1.01, is so prepared that, for temperatures near  $100^{\circ}$ , the density of the whole is nearly that of water. This mixture is placed in a cubical box of sheet-iron, with two holes opposite each other, which are filled with glass, so as to enable the observer to

perceive what is passing within. The box is placed in a metallic envelope, which permits of its being heated laterally. When the temperature of  $120^{\circ}$  has been reached, a large drop of water is allowed to fall into the mixture, which, on reaching the bottom of the box, is partially converted into vapour, and breaks up into a number of smaller drops, some of which take up a position between the two windows, so as to be visible to the observer. The temperature may then be raised to  $140^{\circ}$ ,  $150^{\circ}$ , or even  $180^{\circ}$ , without producing evaporation of any of these drops. Now the maximum tension of steam at  $180^{\circ}$  is equal to 10 atmospheres, and yet we have the remarkable phenomenon of a drop of water remaining liquid at this temperature under no other pressure than that of the external air increased by an inch or two of oil. The reason is that the air necessary to evaporation is not supplied. If the drops be touched with a rod of metal, or, better still, of wood, they are immediately converted into vapour with great violence, accompanied by a peculiar noise. This is explained by the fact that the rods used always carry a certain quantity of condensed air upon their surface, and by means of this air the evaporation is produced. The truth of this explanation is proved by the fact, that when the rods have been used a certain number of times, they lose their power of provoking ebullition, owing, no doubt, to the exhaustion of the air which was adhering to their surfaces.

3. *Production of Ebullition by the formation of Bubbles of Gas in the midst of a Liquid.*—A retort is carefully washed with sulphuric acid, and then charged with water slightly acidulated, from which the air has been expelled by repeated boiling. The retort communicates with a manometer and with an air-pump. The air is exhausted until a pressure of only 150 millimetres is attained, corresponding to  $60^{\circ}$  as boiling-point. Dufour has shown that under these conditions the temperature may be gradually raised to  $75^{\circ}$  without producing ebullition. But if, while things are in this condition, a current of electricity is sent through the liquid by means of two platinum wires previously immersed in it, the bubbles of oxygen and hydrogen which are evolved at the wires immediately produce violent ebullition, and a portion of the liquid is projected explosively, as in Donny's experiment.

From these experiments we may conclude that liquid, when not in contact with gas, has a difficulty in *making a beginning* of vaporization, and may hence remain in the liquid state even at tempera-

tures at which vaporization would upon the whole involve a fall of potential energy.

That vapour (as well as air) can furnish the means of overcoming this difficulty, is established by the fact noted by Professor G. C. Foster,<sup>1</sup> that when a liquid has been boiling for some time in a retort, it sometimes ceases to exhibit the movements characteristic of ebullition, although the amount of vapour evolved at the surface, as measured by the amount of liquid condensed in the receiver, continues undiminished. In these circumstances, it would appear that the superficial layer of liquid, which is in contact with its own vapour, is the only part that is free to vaporize.

The preceding remarks explain the reluctance of water to boil in glass vessels carefully washed, and the peculiar formation, in these circumstances, of large bubbles of steam, causing what is called *boiling by bumping*. In the case of sulphuric acid, the phenomenon is much more marked; if this liquid be boiled in a glass vessel, enormous bubbles are formed at the sides, which, on account of the viscous nature of the liquid, raise the mass of the liquid above them, and then let it fall back with such violence as sometimes to break the vessel. This inconvenience may be avoided by using an annular brazier (Fig. 75), by means of which the upper part only of the liquid is heated.

The ebullition of ether and alcohol presents some similar features, probably because these liquids dissolve the fatty particles on the surface of the glass, and thus adhere to the sides very strongly.

**117. Spheroidal State.**—This is the name given to a peculiar condition which is assumed by liquids when exposed to the action of very hot metals.

If we take a smooth metal plate, and let fall a drop of water upon it, the drop will evaporate more rapidly as the temperature of the plate is increased up to a certain point. When the temperature of the plate exceeds this limit, which, for water, appears to be about



Fig. 75.—Apparatus for Boiling Sulphuric Acid.

<sup>1</sup> Watts's *Dictionary of Chemistry*, art. "Heat," p. 88.

150°, the drop assumes a spheroidal form, rolls about like a ball or spins on its axis, and frequently exhibits a beautiful rippling, as represented in the figure. While in this condition, it evaporates much more slowly than when the plate was at a lower temperature. This latter circumstance is important, and is easily verified by experiment. If the plate be allowed to cool, a moment arrives when the globule of water flattens out, and boils rapidly away with a hissing'noise.



Fig. 76.—Globule in the Spheroidal State.

These phenomena have been long known, and were studied by Leidenfrost and Klaproth; but more complete and searching investigations were made by Boutigny. All liquids are probably capable of assuming the spheroidal state. Among those which have been tested are alcohol, ether, liquid sulphurous acid, and liquid nitrous oxide. When in this state they do not boil. Sometimes bubbles of steam are seen to rise and burst at the top of the globule, but these are always owing to some roughness of the surface, which prevents the steam from escaping in any other way; when the surface is smooth, no bubbles are observed.

If the temperature of the liquid be measured by means of a thermometer with a very small bulb, or a thermo-electric junction, it is always found to be below the boiling-point.

**118. Freezing of Water and Mercury in a Red-hot Crucible.**—This latter property enables us to obtain some very striking and paradoxical results. The boiling-point of liquid sulphurous acid is  $-10^{\circ}$  C., and that of liquid nitrous oxide is about  $-70^{\circ}$  C. If a silver or platinum crucible be heated to redness by a powerful lamp, and some liquid sulphurous acid be then poured into it, this latter assumes the spheroidal state; and drops of water let fall upon it are immediately frozen. Mercury can in like manner be frozen in a red-hot crucible by employing liquid nitrous oxide in the spheroidal state.

These experiments are due to Boutigny, who called attention to them as remarkable exceptions to the usual tendency of bodies to

equilibrium of temperature. The exception is of the same kind as that presented by a vessel of water boiling at a constant temperature of 100° over a hot fire, the heat received by the liquid being in both cases expended in producing evaporation.

**119. The Metal not in Contact with the Liquid.**—The basis of the entire theory of liquids in the spheroidal state is the fact that the liquid and the metal plate do not come into contact. This fact can be proved by direct observation.

The plate used must be quite smooth and accurately levelled. When the plate is heated, a little water is poured upon it, and assumes the spheroidal state. By means of a fine platinum wire which passes into the globule, the liquid is kept at the centre of the metal plate. It is then very easy, by placing a light behind the globule, to see distinctly the space between the liquid and the plate. The appearance thus presented may be easily thrown on a screen by means of the electric light.

The interruption of contact can also be proved by connecting (through a galvanometer) one pole of a battery with the hot plate, while a wire from the other pole is dipped in the liquid. The cur-

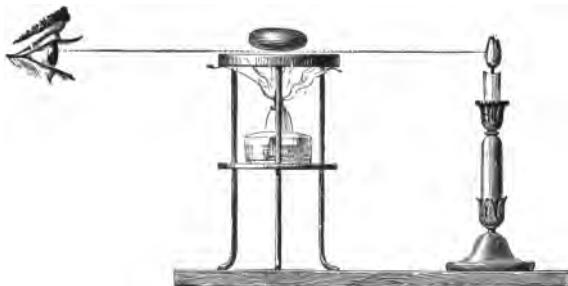


Fig. 77.—Separation between Globule and Plate.

rent refuses to circulate if the liquid is in the spheroidal state, but is immediately established when, on cooling the plate, the liquid begins to boil.

Various attempts have been made to account for the absence of contact between the liquid and the metal, but the true explanation is as yet uncertain.

In consequence of the separation, heat can only pass to the globule by radiation, and hence its comparatively low temperature is accounted for.

The absence of contact between a liquid and a metal at a high

temperature may be shown by several experiments. If, for instance, a ball of platinum be heated to bright redness, and plunged (Fig. 78)

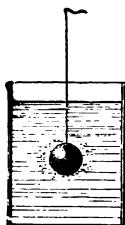


Fig. 78.—Red-hot Ball in Water.

into water, the liquid is seen to recede on all sides, leaving an envelope of vapour round the ball. This latter remains red for several seconds, and contact does not take place till its temperature has fallen to about  $150^{\circ}$ . An active ebullition then takes place, and an abundance of steam is evolved.

Professor Barrett has obtained a more striking effect of the same kind by lowering a red-hot ball of iron into the soapy liquid known as "Plateau's solution."

If drops of melted sugar be let fall on water, they will float for a short time, though their density is greater than that of water, contact being prevented by their high temperature. A similar phenomenon is observed when a fragment of potassium is thrown on water. The water is decomposed; its hydrogen takes fire and burns with a red flame; its oxygen combines with the potassium to form potash; and the globule of potash floats upon the surface without touching it, owing to the high temperature under which it is formed. After a few seconds the globule cools sufficiently to come into contact with the water, and bursts with a slight noise.

**120. Distillation.**—Distillation consists in boiling a liquid and condensing the vapour evolved. It enables us to separate a liquid from the solid matter dissolved in it, and to effect a partial separation of the more volatile constituent of a mixture from the less volatile.

The apparatus employed for this purpose is called a still. One of the simpler forms, suitable for distilling water, is shown in Fig. 79.

It consists of a retort *a*, the neck of which *c* communicates with a spiral tube *dd* called the *worm*, placed in the vessel *e*, which contains cold water. The water in the retort is raised to ebullition, the steam given off is condensed in the worm, and the *distilled water* is collected in the vessel *g*.

As the condensation of the steam proceeds, the water of the cooler becomes heated, and must be renewed; for this purpose a tube descending to the bottom of the cooler is supplied with a continuous stream of cold water from above, while the superfluous water flows out by the tube *i* at the upper part of the cooler. In this way the warm water, which rises to the top, is continually removed. The

boiler is filled about three-quarters full, and the water in it can from time to time be renewed by the opening *f*; but it is advisable not to

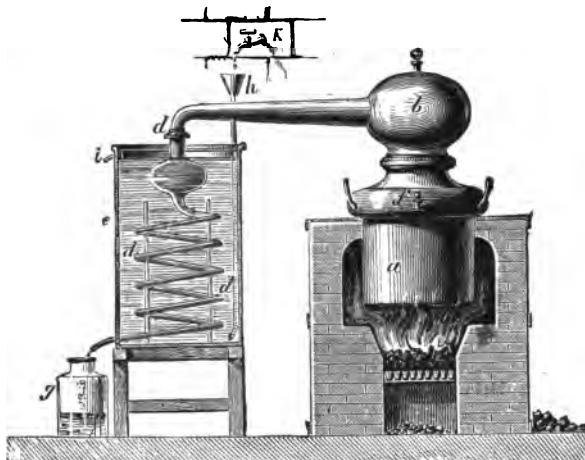


Fig. 79.—Still.

carry the process of distillation too far, and to throw away the liquid remaining in the boiler when its volume has been reduced to a fourth or a fifth of what it was originally. By exceeding this limit we run the risk of impairing the purity of the water by the carrying over of some of the solid matter contained in the liquid in the boiler.

**121. Circumstances which Influence Rapidity of Evaporation.**—In the case of a liquid exposed to the air, and at atmospheric temperature, the rapidity of evaporation increases with the extent of free surface, the dryness of the air, and the rapidity of renewal of the air immediately above the surface.

In the case of a liquid evaporated by boiling, the quantity evaporated in a given time is proportional to the heat received. This depends upon the intensity of the source of heat, the facility with which heat passes through the sides of the vessel, and the area of *heating surface*, that is to say, of surface (or more properly lamina) which is in contact with the liquid on one side, and with the source of heat on the other.

## CHAPTER X.

### QUANTITATIVE MEASUREMENTS RELATING TO VAPOURS.

**122. Pressure of Aqueous Vapour.**—The knowledge of the maximum pressure of the vapour of water at various temperatures is important, not only from a theoretical, but also from a practical point of view, inasmuch as this pressure is the motive force in the steam-engine. Experiments for determining it have accordingly been undertaken by several experimenters in different countries. The researches conducted by Regnault are especially remarkable for the range of temperature which they embrace, as well as for the number of observations which they include, and the extreme precision of the methods employed. Next to these in importance are the experiments of Magnus in Germany and of Fairbairn and Tate in England.

**123. Dalton's Apparatus.**—The first investigations in this subject which have any pretensions to accuracy were those of Dalton. The apparatus which he employed is represented in Fig. 80. Two barometric tubes A and B are inverted in the same cistern H; one is an ordinary barometer, the other a vapour-barometer; that is, a barometer in which a few drops of water have been passed up through the mercury. The two tubes, attached to the support C D, are surrounded by a cylindrical glass vessel containing water which can be raised to different temperatures by means of a fire. The first step is to fill the vessel with ice, and then read the difference of level of the mercury in the two tubes. This can be done by separating the fragments of ice. The difference thus observed is the pressure of aqueous vapour at zero Centigrade. The ice is then replaced by water, and the action of the fire is so regulated as to give different temperatures, ranging between 0° and 100° C., each of which is preserved constant for a few minutes, the water being at the same time well stirred by means of the agitator p q, so as to insure uniformity

of temperature throughout the whole mass. The difference of level in the two barometers is read off in each case; and we have thus the means of constructing, with the aid of graphical or numerical interpolation, a complete table of vapour-pressures from  $0^{\circ}$  to  $100^{\circ}$  C. At or about this latter temperature the mercury in the vapour-barometer falls to the level of the cistern; and the method is therefore inapplicable for higher temperatures. Such a table was constructed by Dalton.

**124. Regnault's Modifications.**—Dalton's method has several defects. In the first place, it is impossible to insure that the temperature shall be everywhere the same in a column as long as that which is formed by the vapour at  $70^{\circ}$ ,  $75^{\circ}$ , and higher temperatures. In the second place, there is always a good deal of uncertainty in observing the difference of level through the sides of the cylindrical glass vessel. Regnault employed this method only up to the temperature of  $50^{\circ}$  C. At this temperature the pressure of the vapour is only about 9 centimetres (less than 4 inches) of mercury, and it is thus unnecessary to heat the barometers throughout their entire length. The improved apparatus is represented in Fig. 81. The two barometric tubes, of an interior diameter of 14 millimetres, traverse two holes in the bottom of a metal box. In one of the sides of the box is a large opening closed with plate-glass, through which the necessary observations can be made with great accuracy. On account of the shortness of the liquid column it was very easy, by bringing a spirit-lamp within different distances of the box, to maintain for a sufficient time any temperature between  $0^{\circ}$  and  $50^{\circ}$  C.

The difference of level between the two mercurial columns should be reduced to  $0^{\circ}$  C. by the ordinary correction. We should also take into consideration the short column of water which is above the



Fig. 80.—Dalton's Apparatus.

mercury in the vapour barometer, and which, by its weight, produces a depression that may evidently be expressed in mercury by dividing the height of the column by 13·59.

To adapt this apparatus to low temperatures, it is modified in the following way. The upper extremity of the vapour barometer tube is drawn out and connected with a small copper tube of three branches, one of which communicates with an air-pump, and another with a glass globe of the capacity of about 500 cubic centimetres. In the interior of this globe is a small bulb of thin glass containing water, from which all the air has been expelled by boiling. The globe is several times exhausted of air, and after each exhaustion is refilled with air which has been passed over desiccating substances. After the last exhaustion, the tube which establishes communication with the air-pump is hermetically sealed, the box is filled with ice, and the pressure at zero of the dry air left behind in the globe by the air-pump is measured; it is of course exceedingly small. Heat is then applied to the globe, the little bulb bursts, and the globe, together with the space above the mercury, is filled with vapour. This form of apparatus can also be employed for temperatures up to 50°, the only difference being that the ice is replaced by water at different temperatures, allowance being made, in each case, for the elastic force of the unexhausted air.

In the case of temperatures below zero, the box is no longer required, and the globe alone is placed in a vessel containing a freezing-mixture. The barometric tubes are surrounded by the air of the apartment.

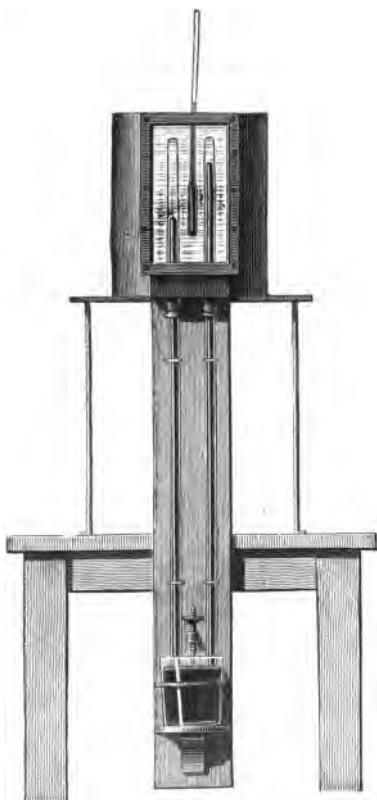


Fig. 81.—Modified Form of Dalton's Apparatus.

In this case the space occupied by the vapour is at two different temperatures in different parts, but it is evident that equilibrium can exist only when the pressure is the same throughout. But, the pressure of the vapour in the globe can never exceed the maximum pressure for the actual temperature; this must therefore be the pressure throughout the entire space, and is consequently that which corresponds to the difference of level observed.

In reality what happens is as follows:—The low temperature of the globe causes some of the vapour to condense; equilibrium is consequently destroyed, a fresh quantity of vapour is produced, enters the globe, and is there condensed, and so on, until the pressure is everywhere the same as the maximum pressure due to the temperature of the globe. This condensation of vapour in the cold part of the space was utilized by Watt in the steam-engine; it is the *principle of the condenser*.

Before Regnault, Gay-Lussac had already turned this principle to account in a similar manner for the measurement of low temperatures.

By using chloride of calcium mixed with successively increasing quantities of snow or ice, the temperature can be brought as low as  $-32^{\circ}$  C. ( $-25.6^{\circ}$  F.), and it can be shown that the pressure of the vapour of water is quite appreciable even at this point.

**125. Measurement of Pressures for Temperatures above  $50^{\circ}$ .**—In investigating the maximum pressure of the vapour of water at temperatures above  $50^{\circ}$ , Regnault made use of the fact that the pressure of the steam of boiling water is equal to the external pressure.

His apparatus consists (Fig. 82) of a copper boiler containing water which can be raised to different temperatures indicated by very delicate thermometers. The vapour produced passes through a tube inclined upwards, which is kept cool by a constant current of water; in this way the experiment can be continued for any length of time, as the vapour formed by ebullition is condensed in the tube, and flows back into the boiler. The tube leads to the lower part of a large reservoir, in which the air can be either rarefied or compressed at will. This reservoir is in communication with a manometer. The apparatus shown in the figure is that employed for pressures not exceeding 5 atmospheres. Much greater pressures, extending to 28 atmospheres, can be attained by simply altering the dimensions of the apparatus without any change in its principle. The manometer employed in this case was the same as that used in testing Boyle's law, consisting of a long column of mercury.

In using this apparatus, the air in the reservoir is first rarefied until the water boils at about  $50^{\circ}$  C.; the occurrence of ebullition being recognized by its characteristic sound, and by the temperature

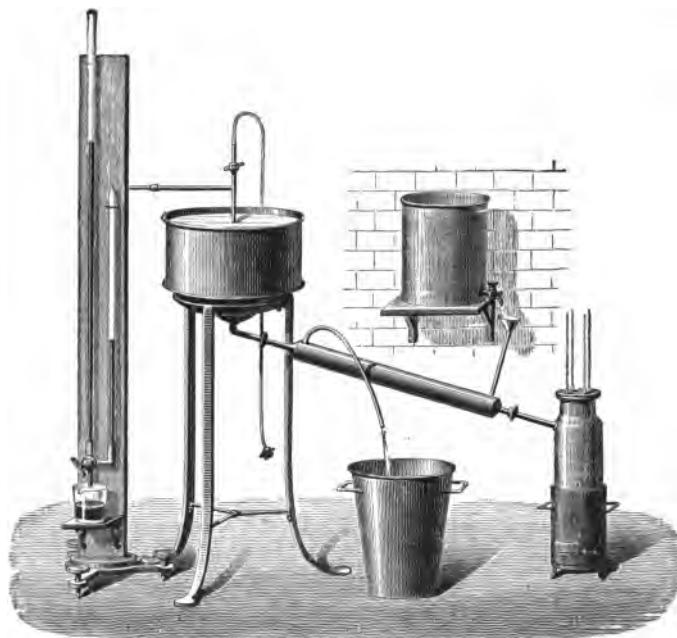


Fig. 82.—Regnault's Apparatus for High Temperatures.

remaining invariable. This steadiness of temperature is of great advantage in making the observations, inasmuch as it enables the thermometers to come into perfect equilibrium of temperature with the water. The pressure indicated by the manometer during ebullition is exactly that of the vapour produced. By admitting air into the reservoir, the boiling-point is raised by successive steps until it reaches  $100^{\circ}$ . After this, air must be forced into the reservoir by a compression-pump.

The following is an abstract of the results thus obtained:—

Temperatures Centigrade.	Pressures in Millimetres of Mercury.	Temperatures Centigrade.	Pressures in Millimetres of Mercury.
- 32° . . . . .	0·32	5° . . . . .	6·53
- 20 . . . . .	0·93	10 . . . . .	9·17
- 10 . . . . .	2·09	15 . . . . .	12·70
- 5 . . . . .	3·11	20 . . . . .	17·39
0 . . . . .	4·60	25 . . . . .	23·55

Temperatures Centigrade.	Pressures in Millimetres of Mercury.	Temperatures Centigrade.	Pressures in Millimetres of Mercury.
30°	31·55	70°	233·09
35	41·82	75	288·51
40	54·91	80	354·64
45	71·39	85	433·04
50	91·98	90	525·45
55	117·47	95	633·77
60	148·70	100	760·00
65	186·94		
Pressures in Atmospheres.		Pressures in Atmospheres.	
100°	1	180°	9·929
121	2·025	189	12·125
134	3·008	199	15·062
144	4·000	213	19·997
152	4·971	225	25·125
159	5·966	230	27·534
171	8·036		

126. *Curve of Steam-pressure.*—The comparison of these pressures with their corresponding temperatures affords no clue to any simple relation between them which might be taken as the physical law of the phenomena. It would appear that the law of variation of maximum pressures is incapable of being thrown into any simple expression—judging at least from the failure of all efforts hitherto made. An attentive examination of the above table will enable us to assert only that the maximum pressure varies more rapidly than the temperature. Thus between 0° and 100° the variation is only 1 atmosphere, but between 100° and 200° it is about 15, and between 200° and 230° about 13 atmospheres.

The clearest way of representing to the mind the law according to which steam-pressure varies with temperature, is by means of a curve whose ordinates represent steam-pressure, while the abscissæ represent the corresponding temperatures. Such a curve is exhibited in Fig. 83. Lengths proportional to the temperatures, reckoned from 0° C., are laid off on the base-line (called the line of abscissæ), and perpendiculars (called ordi-

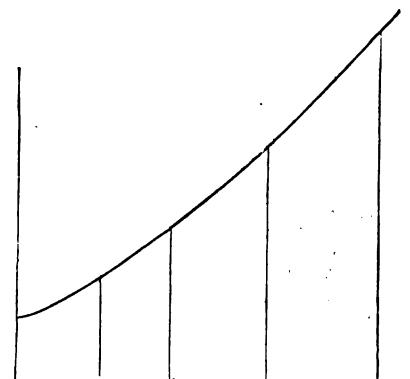


Fig. 83.

nates) are erected at their extremities, the lengths of these perpendiculars being made proportional to the steam-pressure. The scales employed for the two sets of lengths are of course quite independent of one another, their selection being merely a question of convenience. The curve itself is obtained by joining the extremities of the perpendiculars, taking care to avoid sudden changes of direction; and it not only serves to convey to the mind an idea of the amounts of pressure and their rates of variation at different temperatures, but also furnishes the readiest means of determining the pressures at temperatures intermediate between those of observation.

It will be noticed that the curve becomes steeper as the temperature increases, indicating that the pressure increases faster at high than at low temperatures.

**127. Empirical Formulae.**—Though all attempts at finding a rational formula for steam-pressure in terms of temperature have hitherto failed, it is easy to devise empirical formulae which yield tolerably accurate results within a limited range of temperature; and by altering the values of the constants in such a formula by successive steps, it may be adapted to represent in succession the different portions of the curve above described.

The simplest of these approximate formulae<sup>1</sup> is that of Dulong and Arago, which may be written—

$$\left(\frac{40+C}{140}\right)^5 \quad \text{or} \quad \left(\frac{40+F}{252}\right)^5,$$

and gives the maximum pressure *in atmospheres*, corresponding to the temperature C° Centigrade, or F° Fahrenheit. This formula is rigorously correct at 100° C., and gives increasing errors as the temperature departs further from this centre, the errors amounting to about 1½ per cent. at the temperatures 80° C. and 225° C. Hence it appears that between these limits the maximum pressure of aqueous vapour is nearly proportional to the fifth power of the excess of the temperature above –40° C. or –40° F. (for it so happens that this temperature is expressed by the same number on both scales).

**128. Pressures of the Vapours of Different Liquids.**—Dalton held that *the vapours of different liquids have equal pressures at temperatures equally removed from their boiling-points*. Thus the boiling-point of alcohol being 78°, the pressure of alcohol vapour at 70° should be equal to that of the vapour of water at 92°. If this law were correct, it would only be necessary to know the boiling-point

<sup>1</sup> For a general formula, see *Rankine on Steam-engine*, p. 237.

of any liquid in order to estimate the pressure of its vapour at any given temperature; but subsequent experiment has shown that the law is far from being rigorously exact, though it is approximately correct for temperatures differing by only a few degrees from the boiling-points.

Regnault has performed numerous experiments on the vapour-pressure of some of the more volatile liquids, employing for this purpose the same form of apparatus which had served for determining the pressures of aqueous vapour. The following are some of his results:—

VAPOUR OF ALCOHOL.

Temperatures Centigrade.	Pressures in Millimetres.	Temperatures Centigrade.	Pressures in Millimetres.
- 20° . . . . .	3·24	+ 30° . . . . .	78·52
0 . . . . .	12·70	100 . . . . .	1697·55
+ 10 . . . . .	24·23	155 . . . . .	6259·19

VAPOUR OF ETHER.

- 20° . . . . .	68·90	+ 30° . . . . .	634·80
0 . . . . .	184·39	100 . . . . .	4953·80
+ 10 . . . . .	286·83	120 . . . . .	7719·20

VAPOUR OF SULPHIDE OF CARBON.

- 20° . . . . .	47·30	+ 30° . . . . .	434·62
0 . . . . .	127·91	100 . . . . .	3325·15
+ 10° . . . . .	198·46	150 . . . . .	9095·94

**129. Expression of Vapour-pressure in Absolute Measure.**—The maximum pressure of a given vapour at a given temperature is, from its very nature, independent of geographical position, and should therefore, properly speaking, be denoted by one and the same number at all places. This numerical uniformity will not exist if the pressure be expressed, as in the preceding sections, in terms of the length of a column of mercury which balances it. For example, in order to adapt Regnault's determinations to London, we must multiply them by the fraction  $\frac{3456}{3457}$ , inasmuch as 3456 millimetres of mercury exert the same pressure at London as 3457 at Paris. In general, to adapt determinations of pressure made at a place A, to another place B, we must multiply them by the fraction

$$\frac{\text{gravity at A}}{\text{gravity at B}}$$

For if  $h$  denote the height (in centimetres) of a column of mercury at  $0^\circ$ , which produces a pressure  $p$  (dynes per sq. cm.), and  $d$  be the density of mercury at  $0^\circ$ , we have (see *Hydrostatics* in Part I.)

$$p = ghd.$$

Hence, in order that  $p$  may be the same at different places, the values of  $gh$  must be the same; in other words,  $h$  must vary inversely as  $g$ .

**130. Laws of Combination by Volume.**—It was discovered by Gay-Lussac, that when two or more gaseous elements at the same temperature and pressure enter into chemical combination with each other, the two following laws apply:—

1. The volumes of the components bear a very simple ratio to each other, such as 2 to 3, 1 to 2, or 1 to 1.

2. The volume of the compound has a simple ratio to the sum of the volumes of the components.

Ammonia, for example, is formed by nitrogen and hydrogen uniting in the proportion of one volume of the former to three of the latter, and the volume of the ammonia, if reduced to the same pressure as each of its constituents, is just half the sum of their volumes. Further investigation has led to the conclusion (which is now generally received, though hampered by some apparent exceptions), that these laws apply to all cases of chemical combination, the volumes compared being those which would be occupied respectively by the combining elements and the compound which they form, *when reduced to the state of vapour*, at such a temperature and pressure as to be very far removed from liquefaction, and consequently to possess the properties of what we are accustomed to call permanent gases.

It is obvious that if all gases and vapours were equally expansible by heat, the volume-ratios referred to in this law would be the same at all temperatures; and that, in like manner, if they were all equally compressible (whether obeying Boyle's law, or departing equally from it at equal pressures), the volume-ratios would be independent of the pressure at which the comparison was made.

In reality great differences exist between different vapours in both respects, and these inequalities are greater as the vapours are nearer to saturation. It is accordingly found that the above laws of volume-ratio often fail to apply to vapours when under atmospheric pressure and within a few degrees of their boiling-points, and that, in such cases, a much nearer fulfilment of the law is obtained by employing very high temperatures, or operating in inclosures at very low pressures.

**131. Relation of Vapour-densities to Chemical Equivalents.**—Chemists have determined with great accuracy the combining proportions by weight of most of the elements. Hence the preceding laws can

be readily tested for bodies which usually exist in the solid or liquid form, if we are able to compare the densities of their vapours. In fact, if two such elements combine in the ratio, by weight, of  $w_1$  to  $w_2$ , we have

$$v_1 = \frac{w_1}{d_1}, \quad v_2 = \frac{w_2}{d_2},$$

$v_1 v_2 d_1 d_2$  denoting the volumes and densities of the vapours of weights  $w_1 w_2$  of the two substances.

Hence we have the equation—

$$\frac{v_1}{v_2} = \frac{w_1}{w_2} \cdot \frac{d_2}{d_1}$$

which gives the required volume-ratio of the vapours, if the ratio of their densities be known.

The densities themselves will differ enormously according to the pressure and temperature at which they are taken, but their ratio will only vary by comparatively small amounts, and would not differ at all if they were equally expansible by heat, and equally compressible. Hence comparison will be facilitated by tabulating the ratios of the densities to that of some standard gas, namely air, under the same conditions of pressure and temperature, rather than the absolute densities. This is accordingly the course which is generally pursued, so generally indeed, that by the *vapour-density of a substance* is commonly understood the relative density as measured by this ratio.

The process most frequently employed for the determination of this element is that invented by Dumas.

### 132. Dumas' Method.—

The apparatus consists of a glass globe B, containing the substance which is to be converted into vapour.

The globe is placed in a vessel C, containing some liquid which can be raised to a suitable temperature. If the substance to be operated on is one which can be vaporized at 100° C.,

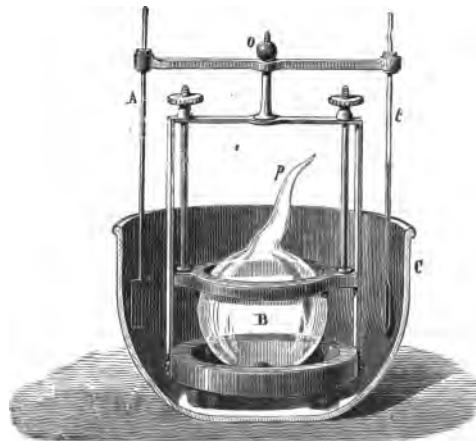


Fig. 84.—Dumas' Apparatus.

the bath consists simply of boiling water. When higher temperatures are required, a saline solution, oil, or a fusible alloy is employed. In all cases, the liquid should be agitated, that its temperature may be the same in all parts. This temperature is indicated by the thermometer  $t$ .

When the substance in the globe has attained its boiling-point, evaporation proceeds rapidly, and the vapour escapes, carrying out the air along with it. When the vapour ceases to issue, we may assume, if the quantity of matter originally taken has been sufficiently large, that all the air has been expelled, and that the globe is full of vapour at the temperature given by the thermometer, and at the external pressure  $H$ . The globe is then hermetically sealed at the extremity  $p$  of the neck, which has been previously drawn out into a fine tube.

**133. Calculation of the Experiment.**—As already remarked, the densities of vapours given in treatises on chemistry express *the ratio of the weight of a given volume of the vapour to that of the same volume of air at the same temperature and pressure*. In order to deduce this ratio from the preceding experiment, we must first find the weight of the vapour. This is done by weighing the globe with its contents, after allowing it to cool. Suppose the weight thus found to be  $W$ . Before the experiment the globe had been weighed full of dry air at a known temperature  $t$  and pressure  $h$ . Suppose this weight to be  $W'$ ; the difference  $W - W'$  evidently represents the excess of the weight of the vapour above that of the air. If, then, we add  $W - W'$  to the weight of the air, we shall evidently have the weight of the vapour. Now the weight of the air is easily deduced from the known volume of the globe. If  $V$  denote this volume at zero expressed in litres, the weight in grammes of the air contained in the globe at the time of weighing is

$$V(1+Kt) 1.293 \times \frac{1}{1+at} \cdot \frac{h}{760}$$

$K$  denoting the coefficient of cubical expansion of glass, and  $a$  the coefficient of expansion of air. The weight of the vapour contained in the globe is consequently

$$A = W - W' + V(1+Kt) \times 1.293 \times \frac{1}{1+at} \cdot \frac{h}{760}$$

Let  $H$  be the pressure and  $T$  the temperature at the time of sealing the globe. The volume occupied by the vapour under these circumstances was  $V(1+KT)$ . The density of the vapour will therefore

be obtained by dividing A by the weight of this volume of air at the same temperature and pressure. But this weight is

$$A' = V(1+KT) \cdot 1.293 \cdot \frac{1}{1+\alpha T} \cdot \frac{H}{760};$$

hence, finally, the required relative density is

$$D = \frac{A}{A'} = \frac{W - W' + V(1+Kt) \cdot 1.293 \cdot \frac{1}{1+\alpha t} \cdot \frac{h}{760}}{V(1+KT) \cdot 1.293 \cdot \frac{1}{1+\alpha T} \cdot \frac{H}{760}}.$$

The correctness of this formula depends upon the assumption that no air is left in the globe. In order to make sure that this condition is fulfilled, the point  $p$  of the neck of the globe is broken off under mercury; the liquid then rushes in, and, together with the condensed vapour, fills the globe completely, if no air has been left behind.

This last operation also affords a means of calculating the volume  $V$ ; for we have only to weigh the mercury contained in the globe, or to measure it in a graduated tube, in order to ascertain its volume at the actual temperature, whence the volume at zero can easily be deduced.

**134. Example.**—In order better to illustrate the method, we shall take the following numerical results obtained in an investigation of the vapour-density of sulphide of carbon:—

Excess of weight of vapour above weight of air,  $W - W' = 3$  gramme; temperature of the vapour  $T = 59^\circ$ ; external pressure  $H = 752.5$  millimetres; volume of the globe at a temperature of  $12^\circ$ , 190 cubic centimetres; temperature of the dry air which filled the globe at the time of weighing,  $t = 15^\circ$ ; pressure  $h = 765$ ;  $K = \frac{1}{38700}$ .

The volume  $V$  of the globe at zero is

$$\frac{190}{1 + \frac{12}{38700}} = 189.94 \text{ cubic centimetres} = 18994 \text{ litre.}$$

The weight of the air contained in the globe is

$$18994 \times 1.293 \cdot \left(1 + \frac{15}{38700}\right) \cdot \frac{1}{1 + 15 \times 0.00366} \cdot \frac{765}{760} = 23442 \text{ gramme.}$$

Weight of the vapour,

$$23442 + W - W' = 23442 \text{ gramme.}$$

The weight of the same volume of air at the same temperature and pressure is

$$18994 \times 1.293 \left(1 + \frac{59}{38700}\right) \cdot \frac{1}{1 + 0.00366 \times 59} \cdot \frac{752.5}{760} = 20019 \text{ gramme.}$$

The density is therefore

$$\frac{53442}{20019} = 2.67.$$

Deville and Troost have effected several improvements in the application of Dumas' method to vapours at high temperatures. These temperatures are obtained by boiling various substances, such as chloride of zinc, cadmium, which boils at  $860^{\circ}$  C., or zinc, which boils at  $1040^{\circ}$  C. For temperatures above  $800^{\circ}$ , the glass globe is replaced by a globe of porcelain, which is hermetically sealed with the oxy-hydrogen blowpipe. The globe itself serves as a pyrometer to determine the temperature; and since the weight of air becomes very inconsiderable at high temperatures, some heavier vapour, such as that of iodine, is substituted in its place. If we suppose, as we may fairly do, that at these high temperatures the coefficient of expansion of the vapour of iodine is the same as that of air, the temperature may easily be deduced from the weight of iodine contained in the globe. We subjoin a table of some relative densities of vapours obtained by this method:—

Water, . . . . .	0·622	Phosphorus, . . . . .	4·5
Alcohol, . . . . .	1·6138	Cadmium, . . . . .	3·94
Ether, . . . . .	2·586	Chloride of aluminium, . . .	9·347
Spirit of turpentine, . . .	5·0180	Bromide of aluminium, . . .	18·62
Iodine, . . . . .	8·716	Chloride of zirconium, . . .	8·1
Sulphur, . . . . .	2·23	Sesquichloride of iron, . . .	11·39

**135. Limiting Values of Relative Densities.**—In investigating the relative density of acetic acid vapour, Cahours found that it went on decreasing as the temperature increased, up to a certain point, beyond which there was no sensible change. A similar circumstance is observed in the case of all substances, only in different degrees. The vapour of sulphur, for instance, has a relative density of 6·65 at  $500^{\circ}$  C., while at about  $1000^{\circ}$  C. it is only 2·23. This indicates that the vapours in question are more expansible by heat than air until the limiting temperatures are attained. It is probable that the nearer a vapour is to its critical point (§ 105) the greater is the change produced in its absolute density by a given change whether of temperature or pressure. The limiting density-ratio is always that which it is most important to determine, and we should consequently take care that the temperature of the vapour is sufficiently high to enable us to obtain it.

**136. Gay-Lussac's Method.**—Gay-Lussac determined the density of the vapour of water and of some other liquids by a method a little

more complicated than that described above, and which for that reason has not been generally adopted in the laboratory. We proceed to describe it, however, on account both of its historical interest and of the importance of the question which it has assisted in solving.

A graduated tube divided into cubic centimetres, suppose, is filled with mercury, and inverted in a cast-iron vessel containing the same liquid. The inverted tube is surrounded by a glass envelope containing water, as in Dalton's apparatus. A small glass bulb containing a given weight  $w$  (expressed in grammes) of distilled water is passed into the tube, and rises to the surface of the mercury. The temperature of the apparatus is then raised by means of a fire below, the bulb bursts, and the water which it contained is converted into vapour. If the quantity of water be not too great, it is all converted into vapour; this is known to be the case when, at the temperature of about  $100^\circ$ , the mercury stands higher in the tube than in the vessel, for if there were any liquid water present, the space would be saturated, and the pressure of the vapour would be equal to the external pressure.

This arrangement accordingly gives the weight of a known volume of the vapour of water. This volume, in cubic centimetres, is  $V(1+KT)$ , where  $V$  denotes the number of divisions of the tube occupied by the vapour, each of which when at the temperature zero represents a cubic centimetre. The temperature  $T$  is marked by a thermometer immersed in the water contained in the envelope. The pressure of the vapour is evidently equal to the external pressure minus the height of the mercury in the tube.

In order to find the relative density, we must divide  $w$  by the weight of a volume  $V(1+KT)$  of air at the temperature  $T$  and pressure  $H-h$ , giving

$$\frac{w}{V(1+KT) \times 0.001293 \times \frac{1}{1+aT} \cdot \frac{H-h}{760}}.$$

It may be remarked that the vapour in this experiment is superheated; but superheated vapour of water obeys Boyle's law, and has

therefore the same relative density as saturated vapour at the same temperature.

The relative density of the vapour of water, as thus determined by Gay-Lussac, is about  $\frac{5}{6}$ , or .625. Several recent investigations have given as a mean result .622, which agrees with the theoretical density deduced from the composition of water.<sup>1</sup>

**137. Meyer's Method.**—Victor Meyer has invented a method of determining vapour densities, which is illustrated by Fig. 86. His apparatus consists of a flask B with a long narrow neck, from which a fine tube branches off near the top, and bends down under

the surface of mercury. A graduated glass jar D filled with mercury can be inverted over the end of the branch tube.

The first operation is to heat the flask by means of a surrounding bath to the temperature at which it is intended to form the vapour. This operation expands the air and expels a portion in bubbles through the mercury. This portion may be allowed to escape into the atmosphere, and when no more bubbles issue, but equilibrium of pressure has been established, the graduated jar is to be inverted over the end of the tube ready for the second operation, which consists in introducing the substance to be vaporized into the flask, the Indian-rubber plug C at the top of the neck being removed for this

purpose and quickly replaced. The formation of the vapour expels more air through the mercury, and this air must be collected in the graduated jar.

Comparing the contents of the flask when this operation has been completed with its contents before the plug was drawn, it is obvious that the vapour has taken the place of air at the same temperature and pressure. The relative vapour density will therefore be the quotient of the mass of the vapour by the mass of the air displaced. The mass of the vapour is known, being the same as that of the

<sup>1</sup> Water is composed of 2 volumes of hydrogen, and 1 volume of oxygen, forming 2 volumes of vapour of water. The sum of the density of oxygen and twice the density of hydrogen is 1.244, and the half of this is exactly .622.—D.



Fig. 86.—Meyer's Apparatus.

substance introduced into the flask; and the mass of the air displaced is known, being the same as that of the air collected in the graduated jar. In the figure, A represents a small tube containing the substance to be vaporized, and asbestos is placed at the bottom of the flask to prevent the latter from being broken when this tube is dropped in.

**138. Volume of Vapour formed by a given Weight of Water.**—When the density of the vapour of water is known, the increase of volume which occurs when a given quantity of water passes into the state of vapour may easily be calculated. Suppose, for instance, that we wish to find the volume which a cubic centimetre of water at 4° will occupy in the state of vapour at 100°. At this temperature the pressure of the vapour is equal to one atmosphere, and its weight is equal to .622 times the weight of the same volume of air at the same temperature and pressure. If then V be the volume in litres, we have (in grammes)

$$V \times 1.293 \times \frac{1}{1+100\alpha} \times .622 = 1,$$

whence

$$V = \frac{1+100\alpha}{1.293 \times .622} = \frac{1.366}{.804246} = 1.698 \text{ lit.} = 1698 \text{ cubic centimetres.}$$

Hence we see that water at 4° gives about 1700 times its volume of vapour at 100° C.

The latent heat of evaporation is doubtless connected with this increase of volume; and it may be remarked that both these elements appear to be greater for water than for any other substance.

**139. Heat of Evaporation.**—The latent heat of evaporation of water, and of some other liquids, can be determined by means of Despretz's apparatus, which is shown in Fig. 87.

The liquid is boiled in a retort C, which is connected with a worm S surrounded by cold water, and terminating in the reservoir R. The vapour is condensed in the worm, and collects in the reservoir, whence it can be drawn by means of the stop-cock r. The tube T, which is fitted with a stop-cock r', serves to establish communication between the reservoir and the atmosphere, or between the reservoir and a space where a fixed pressure is maintained, so as to produce ebullition at any temperature required, as indicated by the thermometer t. A is an agitator for keeping the water at a uniform temperature, indicated by the thermometer t'.

In using the apparatus, the first step is to boil the liquid in the

retort, and when it is in active ebullition, it is put in communication with the worm. The temperature of the calorimeter has previously been lowered a certain number of degrees below that of the surrounding air, and the experiment ceases when it has risen to the same number of degrees above. The compensation may thus be considered as complete, since the rate of heating is nearly uniform.

If  $W$  be the equivalent of the calorimeter in water,  $t$  its initial temperature,  $\theta$  its final temperature; then the quantity of heat gained by it is  $W(\theta - t)$ . This heat comes partly from the latent heat disengaged at the moment of condensation of the vapour, partly from the loss of temperature of the condensed water, which sinks from  $T$ , the boiling-point of the liquid, to the temperature of the calorimeter. If, then,  $x$  denote the latent heat of evaporation.  $w$  the weight of the

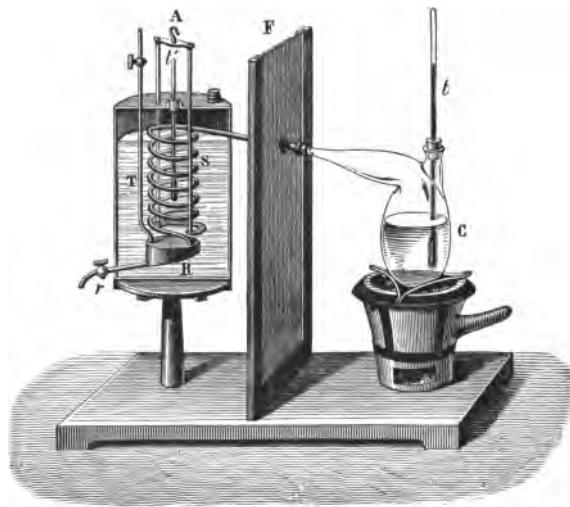


Fig. 87.—Despretz's Apparatus.

liquid collected in the box  $R$ , and  $c$  its specific heat, we have the equation

$$W(\theta - t) = wx + wc(T - \theta).$$

This experiment is exposed to some serious causes of error. The calorimeter may be heated by radiation from the screen  $F$  which protects it from the direct radiation of the furnace. Heat may also be propagated by means of the neck of the retort. Again, the vapour is not dry when it passes into the worm, but carries with it small

drops of liquid. Finally, some of the vapour may be condensed at the top of the retort, and so pass into the worm in a liquid state. This last objection is partly removed by sloping the neck of the retort upwards from the fire, but it sometimes happens that this precaution is not sufficient.

**140. Regnault's Experiments.**—The labours of Regnault in connection with the subject of latent heat are of the greatest importance, and have resulted in the elaboration of a method in which all these sources of error are entirely removed. The results obtained by him are the following:—

The quantity of heat required to convert a gramme of water at  $100^{\circ}$  into vapour, without change of temperature, is 537 grammē-degrees.

If the water were originally at zero, the total amount of heat required to raise it to  $100^{\circ}$  and then convert it into vapour would evidently be 637 grammē-degrees; and it is this total amount which is most important to know in the application of heat in the arts.

In general, if  $Q$  denote the total quantity of heat<sup>1</sup> required to raise water from zero to the temperature  $T$ , and then convert it into vapour at this temperature, the value of  $Q$  may be deduced with great exactness from the formula

$$Q = 606.5 + .305T. \quad (a)$$

From what we have said above, it will be seen that if  $\lambda$  denote the latent heat of evaporation at temperature  $T$ , we must have

$$Q = \lambda + T,$$

whence, by substituting for  $Q$  in (a), we have

$$\lambda = 606.5 - .695T. \quad (b)$$

Hence it appears that latent heat varies in the opposite direction to temperature. This fact had been previously discovered by Watt; but he went too far, and maintained that the increase of the one was *equal* to the diminution of the other, or, in his own words, that “the sum of the sensible and latent heats” (that is  $T + \lambda$ ) “is constant.” From (a) we can find the total heat for any given temperature, and from (b) the latent heat of evaporation at any given tem-

<sup>1</sup> Called by Regnault the total heat of saturated vapour at  $T^{\circ}$ , or the total heat of vaporization at  $T^{\circ}$ .

perature. The results for every tenth degree between  $0^{\circ}$  and  $230^{\circ}$  are given in the following table:—

Temperatures Centigrade.	Latent Heat.	Total Heat.	Temperatures Centigrade.	Latent Heat.	Total Heat.
0° . . . . .	606	606	120° . . . . .	522	642
10 . . . . .	600	610	130 . . . . .	515	645
20 . . . . .	593	613	140 . . . . .	508	648
30 . . . . .	586	616	150 . . . . .	501	651
40 . . . . .	579	619	160 . . . . .	494	654
50 . . . . .	572	622	170 . . . . .	486	656
60 . . . . .	565	625	180 . . . . .	479	659
70 . . . . .	558	628	190 . . . . .	472	662
80 . . . . .	551	631	200 . . . . .	464	664
90 . . . . .	544	634	210 . . . . .	457	667
100 . . . . .	537	637	220 . . . . .	449	669
110 . . . . .	529	639	230 . . . . .	442	672

To reduce latent heat and total heat from the Centigrade to the Fahrenheit scale, we must multiply by  $\frac{9}{5}$ . Thus the latent and total heat of steam at  $212^{\circ}$  F. are  $966\cdot6$  and  $1146\cdot6$ . Total heat is here reckoned from  $32^{\circ}$  F. If we reckon it from  $0^{\circ}$  F., 32 must be added.

The following table taken from the researches of Favre and Silbermann, gives the latent heat of evaporation of a number of liquids at the temperature of their boiling-point, referred to the Centigrade scale:—

	Boiling- point.	Latent Heat.		Boiling- point.	Latent Heat.
Wood-spirit, . . .	66·5°	264	Acetic acid, . . . . .	120°	102
Absolute alcohol, . .	78	208	Butyric acid, . . . . .	164	115
Valeric alcohol, . .	78	121	Valeric acid, . . . . .	175	104
Ether, . . . . .	38	91	Acetic ether, . . . . .	74	100
Ethal, . . . . .	38	58	Oil of turpentine, . . . . .	156	69
Valeric ether, . . .	113·5	113·5	Essence of citron, . . . . .	165	70
Formic acid, . . .	100	169			

## CHAPTER XI.

### HYGROMETRY.

141. **Humidity.**—The condition of the air as regards moisture involves two elements:—(1) the amount of vapour present in the air, and (2) the ratio of this to the amount which would saturate the air at the actual temperature. It is upon the second of these elements that our sensations of dryness and moisture chiefly depend, and it is this element which meteorologists have agreed to denote by the term *humidity*; or, as it is sometimes called, *relative humidity*. It is usually expressed as a percentage.

The words *humid* and *moist*, as applied to air in ordinary language, nearly correspond to this technical use of the word *humidity*; and air is usually said to be dry when its *humidity* is considerably below the average. In treatises on physics, “dry air” usually denotes air whose *humidity* is zero.

The air in a room heated by a hot stove contains as much vapour weight for weight as the open air outside; but it is drier, because its capacity for vapour is greater. In like manner the air is drier at noon than at midnight, though the amount of vapour present is about the same; and it is for the most part drier in summer than in winter, though the amount of vapour present is much greater.

It is to be borne in mind that a cubic foot of air is able to take up the same amount of vapour as a cubic foot of empty space; and “relative humidity” may be defined as *the ratio of the mass of vapour actually present in a given space, to the mass which would saturate the space at the actual temperature*.

Since aqueous vapour fulfils Boyle’s law, these masses are proportional to the vapour-pressure which they produce, and relative humidity may accordingly be defined as *the ratio of the actual*

vapour-pressure to the maximum vapour-pressure for the actual temperature.

**142. Simultaneous Changes in the Dry and Vaporous Constituents.**—When a mixture of air and vapour is subjected to changes of temperature, pressure, or volume which do not condense any of its vapour, the two constituents are similarly affected, since they have both the same coefficient of expansion, and they both obey Boyle's law. If the volume of the whole be reduced from  $v_1$  to  $v_2$  at constant temperature, both the densities will be multiplied by  $\frac{v_1}{v_2}$ , and hence, by Boyle's law, the pressures will also be multiplied by  $\frac{v_1}{v_2}$ . If, on the other hand, the temperature be altered from  $t_1$  to  $t_2$  without change of volume, both the pressures will be multiplied by  $\frac{1+at_2}{1+at_1}$ . The ratio of the vapour-pressure to the dry-air pressure remains unchanged in both cases.

If the changes of volume and temperature are effected simultaneously, each of the pressures will be multiplied by  $\frac{v_1}{v_2} \frac{1+at_2}{1+at_1}$ , and the total pressure will be multiplied by the same factor. If the total pressure remains unchanged, as is the case when there is free communication between the altered air and the general atmosphere, both the dry-air pressure and the vapour-pressure will therefore remain unchanged.

**143. Dew-point.**—When a mixture of dry air and vapour is cooled down at constant pressure until the vapour is at saturation, the temperature at which saturation occurs is called the *dew-point* of the original mass; and if the mixture be cooled below the dew-point, some of the vapour will be condensed into liquid water or solid ice.

The reasoning of the preceding section shows that the process of cooling down to the dew-point does not alter the vapour-pressure. The *actual vapour-pressure* in any portion of air is therefore *equal to the maximum vapour-pressure at the dew-point*.

When air is confined in a close vessel, and cooled at constant volume, its pressure and density at any given temperature, and the pressures and densities of its dry and vaporous constituents, will be less than if it were in free communication with the atmosphere. Hence its vapour will not be at saturation when cooled down to what is above defined as the dew-point of the original mass, but a lower temperature will be requisite.

**144.** These conclusions can also be established as follows:—

Let  $P$  denote the pressure of the mixture,  
 $p$      "     the pressure of the vaporous constituent,  
 $V$      "     the volume,  
 $T$      "     the temperature reckoned from absolute zero on the air thermometer.

Then for all changes which do not condense any of the vapour

$$\frac{VP}{T} \text{ is constant, and } \frac{Vp}{T} \text{ is constant.}$$

When  $P$  is also constant, we have  $\frac{V}{T}$  constant, and therefore  $p$  constant.

On the other hand, when  $V$  is constant,  $p$  will vary as  $T$ , and will diminish as  $T$  diminishes.

**145. Hygoscopes.**—Anything which serves to give rough indications of the state of the air as regards moisture may be called a *hygroscope* (*hypoc*, moist). Many substances, especially those which are composed of organic tissue, have the property of absorbing the moisture of the surrounding air, until they attain a condition of equilibrium such that their affinity for the moisture absorbed is exactly equal to the force with which the latter tends to evaporate. Hence it follows that, according to the dampness or dryness of the air, such a substance will absorb or give up vapour, either of which processes is always attended with a variation in the dimensions of the body. The nature of this variation depends upon the peculiar structure of the substance; thus, for instance, bodies formed of filaments exhibit a greater increase in the direction of their breadth than of their length. Membranous bodies, on the other hand, such as paper or parchment, formed by an interlacing of fibres in all directions, expand or contract almost as if they were homogeneous. Bodies composed of twisted fibres, as ropes and strings, swell under the action of moisture, grow shorter, and are more tightly twisted. The opposite is the case with catgut, which is often employed in popular hygoscopes.

**146. Hygrometers.**—Instruments intended for furnishing precise measurements of the state of the air as regards moisture are called *hygrometers*. They may be divided into four classes:—

1. Hygrometers of absorption, which should rather be called hygoscopes.
2. Hygrometers of condensation, or dew-point instruments.
3. Hygrometers of evaporation, or wet and dry bulb thermometers.

4. Chemical hygrometers, for directly measuring the weight of vapour in a given volume of air.

**147. De Saussure's Hygrometer.**—The best hygrometer of absorption is that of De Saussure, consisting of a hair deprived of grease, which by its contractions moves a needle (Fig. 88). When the hair relaxes, the needle is caused to move in the opposite direction

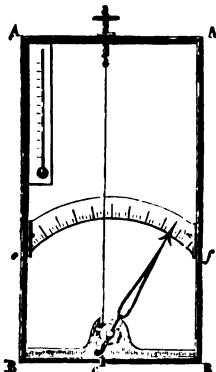


Fig. 88.—De Saussure's Hygrometer.



Fig. 89.—Monnier's Hygrometer.

by a weight, which serves to keep the hair always equally tight. The hair contracts as the humidity increases, but not in simple proportion, and Regnault's investigations have shown that, unless the most minute precautions are adopted in the construction and graduation of each individual instrument, this hygrometer will not furnish definite numerical measures.

Fig. 89 represents Monnier's modification of De Saussure's hygrometer, in which the hair, after passing over four pulleys, is attached to a light spring, which serves instead of a weight, and gives the advantage of portability.

These instruments are never employed for scientific purposes in this country.

**148. Dew-point Hygrometers.**—These are instruments for the direct observation of the dew-point, by causing moisture to be condensed from the air upon the surface of a body artificially cooled to a known temperature.

The dew-point, which is itself an important element, gives directly, as we have seen in § 148, the pressure of vapour; and if the temperature of the air is at the same time observed, the pressure requisite for saturation is known. The ratio of the former to the latter is the humidity.

**149. Dines' Hygrometer.**—One of the best dew-point hygrometers is that invented by the late Mr. Dines, shown both in perspective and in section in Figs. 90, 91. Cold water, with ice, if necessary, is put into the reservoir A, and by turning on the tap B this water is allowed to flow through the pipe C into the small double chamber D, the top of which, E, is formed of thin black glass, on which the smallest film of dew is easily perceived. After flowing under the black glass and around the bulb of a thermometer which lies immediately below it, the water escapes through a discharge pipe, and can be received in a vessel, from which it may again be poured into the reservoir A. As soon as any dew is seen on the black glass, the thermometer should be read, and the tap turned off, or partly off, until the dew disappears, when a second reading of the thermometer should be taken.

The mean of the two will be approximately the dew-point; and in order to obtain a good determination, matters should be so managed as to make the temperatures of appearance and disappearance nearly identical.

**150. Daniell's Hygrometer.**—Daniell's hygrometer has been very extensively used. It consists of a bent tube with a globe at each end, and is partly filled with ether. The rest of the space is occupied with vapour of ether, the air having been expelled. One of the globes A is made of black glass, and contains a thermometer *t*. The method of using the instrument is as follows:—The whole of the liquid is first passed into the globe A, and then the other globe B, which is covered with muslin, is moistened externally with ether.

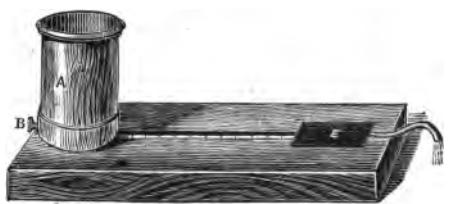


Fig. 90.—Dines' Hygrometer.



SECTION  
Fig. 91.—Dines' Hygrometer.

The evaporation of this ether from the muslin causes a condensation of vapour of ether in the interior of the globe, which produces

a fresh evaporation from the surface of the liquid in A, thus lowering the temperature of that part of the instrument. By carefully watching the surface of the globe, the exact moment of the deposition of dew may be ascertained. The temperature is then read on the inclosed thermometer.

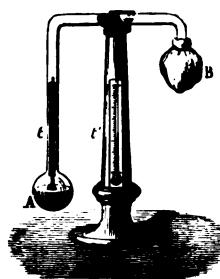


Fig. 92.  
Daniell's Hygrometer.

If the instrument be now left to itself, the exact moment of the disappearance of the dew may be observed; and the usual plan is to take the mean between this temperature and that first observed. The temperature of the surrounding air is given by a thermometer  $t'$  attached to the stand.

**151. Regnault's Hygrometer.**—Regnault's hygrometer consists (Fig. 93) of a glass tube closed at the bottom by a very thin silver cap D. The opening at the upper end is closed by a cork, through which

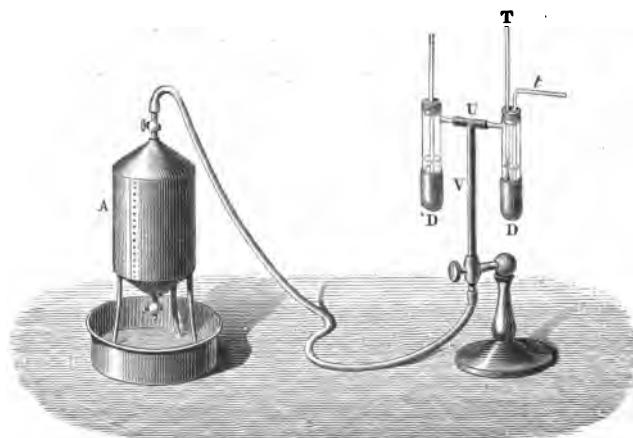


Fig. 93.—Regnault's Hygrometer.

passes the stem of a thermometer T, and a glass tube  $t$  open at both ends. The lower end of the tube and the bulb of the thermometer dip into ether contained in the silver cap. A side tube establishes communication between this part of the apparatus and a vertical

tube UV, which is itself connected with an aspirator<sup>1</sup> A, placed at a convenient distance. By allowing the water in the aspirator to escape, a current of air is produced through the ether, which has the effect of keeping the liquid in agitation, and thus producing uniformity of temperature throughout the whole. It also tends to hasten evaporation; and the cold thus produced speedily causes a deposition of dew, which is observed from a distance with a telescope, thus obviating the risk of vitiating the observation by the too close proximity of the observer. The observation is facilitated by the contrast offered by the appearance of the second cap, which has no communication with the first, and contains a thermometer for giving the temperature of the external air. By regulating the flow of liquid from the aspirator, the temperature of the ether can be very nicely controlled, and the dew can be made to appear and disappear at temperatures nearly identical. The mean of the two will then very accurately represent the dew-point.

The liquid employed in Regnault's hygrometer need not be ether. Alcohol, a much less volatile liquid, will suffice. This is an important advantage; for, since the boiling-point of ether is 36° C. (97° F.), it is not easy to preserve it in hot climates.

**152. Wet and Dry Bulb Hygrometer.—** This instrument, which is also called Mason's hygrometer, and is known on the Continent as August's psychrometer, consists (Fig. 94) of two precisely similar thermometers, mounted at a short distance from each other, the bulb of one of them being covered with muslin, which is kept moist by means of a cotton wick leading from a vessel of water. The evaporation which takes place from the moistened bulb produces a depression of temperature, so that this thermometer reads lower than the other by an amount which increases with the dryness of the air. The instrument must be mounted in such a way that the air can circulate



Fig. 94.  
Wet and Dry Thermometers.

<sup>1</sup> An aspirator is a vessel into which air is sucked at the top to supply the place of water which is allowed to escape at the bottom; or, more generally, it is any apparatus for sucking in air or gas.

very freely around the wet bulb; and the vessel containing the water should be small, and should be placed some inches to the side. The level of this vessel must be high enough to furnish a supply of water which keeps the muslin thoroughly moist, but not high enough to cause drops to fall from the bottom of the bulb. Unless these precautions are observed, the depression of temperature will not be sufficiently great, especially in calm weather.

In frosty weather the wick ceases to act, and the bulb must be dipped in water some time before taking an observation, so that all the water on the bulb may be frozen, and a little time allowed for evaporation from the ice, before the reading is taken.

The great facility of observation afforded by this instrument has brought it into general use, to the practical exclusion of other forms of hygrometer. As the theoretical relation between the indications of its two thermometers and the humidity as well as the dew-point of the air is rather complex, and can scarcely be said to be known with certainty, it is usual, at least in this country, to effect the reduction by means of tables which have been empirically constructed by comparison with the indications of a dew-point instrument. The tables universally employed by British observers were constructed by Mr. Glaisher, and are based upon a comparison of the simultaneous readings of the wet and dry bulb thermometers and of Daniell's hygrometer taken for a long series of years at Greenwich observatory, combined with some similar observations taken in India and at Toronto.<sup>1</sup>

According to these tables, the difference between the dew-point and the wet-bulb reading bears a constant ratio to the difference between the two thermometers, when the temperature of the dry-bulb thermometer is given. When this temperature is 53° F., the dew-point is as much below the wet-bulb as the wet-bulb is below the temperature of the air. At higher temperatures the wet-bulb reading is nearer to the dew-point than to the air-temperature, and the reverse is the case at temperatures below 53°.

153. In order to obtain a clue to the construction of a rational formula for deducing the dew-point from the indications of this instrument, we shall assume that the wet-bulb is so placed that its temperature is not sensibly affected by radiation from surrounding objects, and hence that the heat which becomes latent by the

<sup>1</sup> The first edition of these Tables differs considerably from the rest, and is never used; but there has been no material alteration since the second edition (1856).

evaporation from its surface is all supplied by the surrounding air. When the temperature of the wet-bulb is falling, heat is being consumed by evaporation faster than it is supplied by the air; and the reverse is the case when it is rising. It will suffice to consider the case when it is stationary, and when, consequently, the heat consumed by evaporation in a given time is exactly equal to that supplied by the air.

Let  $t$  denote the temperature of the air, which is indicated by the dry-bulb thermometer;  $t'$  the temperature of the wet-bulb;  $T$  the temperature of the dew-point, and let  $f, f', F$  be the vapour-pressures corresponding to saturation at these three temperatures. Then, as shown in § 143, the tension of the vapour present in the air at its actual temperature  $t$  is also equal to  $F$ .

We shall suppose that wind is blowing, so that continually fresh portions of air come within the sphere of action of the wet-bulb. Then each particle of this air experiences a depression of temperature and an increase of vapour-pressure as it comes near the wet-bulb, from both of which it afterwards recovers as it moves away and mixes with the general atmosphere.

If now it is legitimate to assume<sup>1</sup> that this depression of temperature and exaltation of vapour-pressure are always proportional to one another, not only in comparing one particle with itself at different times, but also in comparing one particle with another, we have the means of solving our problem; at all events, if we may make the additional assumptions that a portion of the air close to the wet-bulb is at the temperature of the wet-bulb, and is saturated.

On these assumptions the greatest reduction of temperature of the air is  $t - t'$ , and the greatest increase of vapour-pressure is  $f' - F$ , and the corresponding changes in the whole mass are proportional to these. The three temperatures  $t, t', T$  must therefore be so related, that the heat lost by a mass of air in cooling through the range  $t - t'$ , is just equal to the heat which becomes latent in the formation of as much vapour as would raise the vapour-pressure of the mass by the amount  $f' - F$ .

<sup>1</sup> The assumption which Dr. Apjohn actually makes is as follows:—"When in the moist-bulb hygrometer the stationary temperature is attained, the caloric which vaporizes the water is necessarily exactly equal to that which the air imparts in descending from the temperature of the atmosphere to that of the moistened bulb; and the air which has undergone this reduction becomes saturated with moisture" (*Trans. R.I.A.*. Nov. 1834).

This implies that all the air which is affected at all is affected to the maximum extent—a very harsh supposition; but August independently makes the same assumption.

Let  $h$  denote the height of the barometer,  $s$  the specific heat of air,  $D$  the relative density of vapour (§ 131),  $L$  the latent heat of steam, and let the vapour-pressures be expressed by columns of mercury.

Then the mass of the air is to that of the vapour required to produce the additional tension, as  $h$  to  $D (f' - F)$ , and we are to have

$$LD(f' - F) = s(t - t')h,$$

or

$$f' - F = (t - t')h \cdot \frac{s}{LD}, \quad (1)$$

which is the required formula, enabling us, with the aid of a table of vapour-pressures, to determine  $F$ , and therefore the dew-point  $T$ , when the temperatures  $t, t'$  of the dry and wet bulb, and the height  $h$  of the barometer, have been observed. The expression for the relative humidity will be  $\frac{T}{f'}$ .

Properly speaking,  $s$  denotes the specific heat not of dry air but of air containing the actual amount of vapour, and therefore depends to some extent upon the very element which is to be determined; but its variation is inconsiderable.  $L$  also varies with the known quantity  $t'$ , but its variations are also small within the limits which occur in practice. The factor  $\frac{s}{LD}$  may therefore be regarded as constant, and its value, as adopted by Dr. Apjohn<sup>1</sup> for the Fahrenheit scale, is  $\frac{1}{2610}$  or  $\frac{1}{30} \times \frac{1}{87}$ . We thus obtain what is known as *Apjohn's formula*,

$$F = f' - \frac{t - t'}{87} \cdot \frac{h}{30}. \quad (2)$$

When the wet-bulb is frozen,  $L$  denotes the sum of the latent heats of liquefaction and vaporization, and the formula becomes

$$F = f' - \frac{t - t'}{96} \cdot \frac{h}{30}. \quad (3)$$

<sup>1</sup> This value was founded on the best determinations which had been made at the time, the specific heat of air being taken as .267, the value obtained by Delaroche and Berard. The same value was employed by Regnault in his hygrometrical investigations. At a still later date Regnault himself investigated the specific heat of air and found it to be .237. When this correct value is introduced into Regnault's theoretical formula (which is substantially the same as Apjohn's), the discrepancies which he found to exist between calculation and observation are increased, and amount, on an average, to about 25 per cent of the difference between wet-bulb temperature and dew-point. The inference is that the assumptions on which the theoretical formulæ are based are not accurate; and the discrepancy is in such a direction as to indicate that diffusion of heat is more rapid than diffusion of vapour.

In calm weather, and also in very dry weather, the humidity, as deduced from observations of wet and dry thermometers, is generally too great, probably owing mainly to the radiation from surrounding objects on the wet-bulb, which makes its temperature too high.

**154. Chemical Hygrometer.**—The determination of the quantity of aqueous vapour in the atmosphere may be effected by ordinary chemical analysis in the following manner:—

An aspirator A, of the capacity of about 50 litres, communicates at its upper end with a system of U-tubes 1, 2, 3, 4, 5, 6, filled with

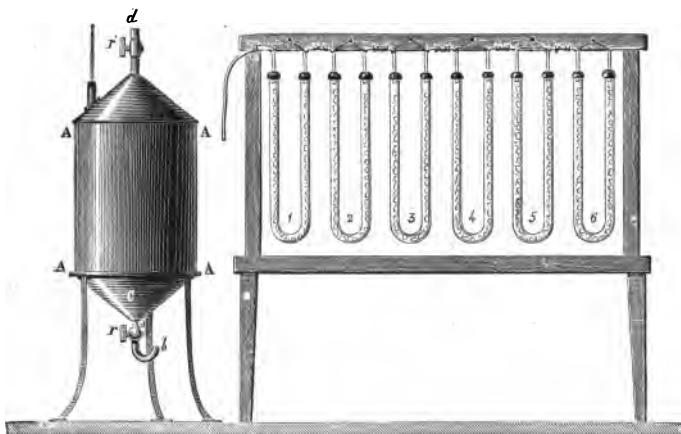


Fig. 95.—Chemical Hygrometer.

pieces of pumice soaked in sulphuric acid. The aspirator being full of water, the stop-cock at the bottom is opened, and the air which enters the aspirator to take the place of the water is obliged to pass through the tubes, where it leaves all its moisture behind. This moisture is deposited in the first tubes only. The last tube is intended to absorb any moisture that may come from the aspirator. Suppose  $w$  to be the increase of weight of the first tubes 4, 5, 6; this is evidently the weight of the aqueous vapour contained in the air which has passed through the apparatus. The volume  $V$  of this air, which we will suppose to be expressed in litres, may easily be found by measuring the amount of water which has escaped. This air has been again saturated by contact with the water of the aspirator, and the aqueous vapour contained in it is consequently at the maximum pressure corresponding to the temperature indicated by a thermometer attached to the apparatus. Let this pressure be denoted

by  $f$ . The volume occupied by this air when in the atmosphere, where the temperature is  $T$ , is known by the regular formulæ to have been

$$V \cdot \frac{H-f}{H-x} \cdot \frac{1+at}{1+at},$$

$x$  denoting the pressure of the aqueous vapour in the atmosphere, and  $H$  the total atmospheric pressure as indicated by the barometer; and, since the relative density of steam is .622, and the weight of a litre of air at temperature 0° C. and pressure 760 mm. is 1.293 gramme, the weight of vapour which this air contained must have been

$$V \cdot \frac{H-f}{H-x} \cdot \frac{1+at}{1+at} \times 1.293 \times .622 \cdot \frac{x}{760} \cdot \frac{1}{1+at},$$

which must be equal to the known weight  $w$ , and thus we have an equation from which we find

$$x = \frac{w(1+at)760H}{V(H-f) \times .622 \times 1.293 + w(1+at)760}.$$

A good approximation will be obtained by writing

$$w = V \times 1.293 \times .622 \frac{x}{760}.$$

whence

$$x = 945 \frac{w}{V}.$$

This method has all the exactness of a regular chemical analysis, but it involves great labour, and is, besides, incapable of showing the sudden variations which often occur in the humidity of the atmosphere. It can only give the mean quantity of moisture in a given volume of air during the time occupied by the experiment. Its accuracy, however, renders it peculiarly suitable for checking the results obtained by other methods, and it was so employed by Regnault in the investigations to which we have referred in the footnote to the preceding section.

**155. Weight of a given Volume of Moist Air.**—The laws of vapours and the known formulæ of expansion enable us to solve a problem of very frequent occurrence, namely, the determination of the weight of a given volume of moist air. Let  $V$  denote the volume of this air,  $H$  its pressure,  $f$  the pressure of the vapour of water in it, and  $t$  its temperature. The entire gaseous mass may be divided into two parts, a volume  $V$  of dry air at the temperature  $t$  and the pressure  $H-f$ , whose weight is, by known formulæ,

$$V \times 1.293 \times \frac{1}{1+at} \cdot \frac{H-f}{760},$$

and a volume  $V$  of aqueous vapour at the temperature  $t$  and the pressure  $f$ ; the weight of this latter is

$$\frac{5}{8}V \times 1.293 \times \frac{1}{1+at} \cdot \frac{f}{760}.$$

The sum of these two weights is the weight required, viz.

$$V \times 1.293 \times \frac{1}{1+at} \cdot \frac{H - \frac{3}{8}f}{760}$$

**156. Ratio of the Volumes occupied by the same Air when saturated at Different Temperatures and Pressures.**—Suppose a mass of air to be in presence of a quantity of water which keeps it always saturated; let  $H$  be the total pressure of the saturated air,  $t$  its temperature, and  $V$  its volume.

At a different temperature and pressure  $t'$  and  $H'$ , the volume occupied  $V'$  will in general be different. The two quantities  $V$  and  $V'$  may be considered as the volumes occupied by a mass of dry air at temperatures  $t$  and  $t'$  and pressures  $H-f$  and  $H'-f'$ ; we have then the relation

$$\frac{V}{V'} = \frac{H'-f'}{H-f} \cdot \frac{1+at}{1+at'} \quad (1)$$

In passing from one condition of temperature and pressure to another, it may be necessary, for the maintenance of saturation, that a new quantity of vapour should be formed, or that a portion of the vapour should be condensed, or again, neither the one nor the other change may take place. To investigate the conditions on which these alternatives depend, let  $D$  and  $D'$  be the maximum densities of vapour at the temperatures  $t$  and  $t'$  respectively. Suppose we have  $t' > t$ , and that, without altering the pressure  $f$ , the temperature of the vapour is raised to  $t'$ , all contact with the generating liquid being prevented. The vapour will no longer remain saturated; but, on increasing the pressure to  $f'$ , keeping the temperature unchanged, saturation will again be produced. This latter change does not alter the actual quantity of vapour, and if we suppose its coefficient of expansion to be the same as that of air, we shall have

$$\frac{D}{D'} = \frac{f}{f'} \cdot \frac{1+at'}{1+at}, \quad (2)$$

and, by multiplying together equations (1) and (2), we have

$$\frac{VD}{V'D'} = \frac{H'f - f'}{Hf' - f}. \quad (3)$$

From this result the following particular conclusions may be deduced:—

1. If  $H'f = H_f'$ ,  $VD = VD'$ , that is, the mass of vapour is the same in both cases; consequently, neither condensation nor evaporation takes place.

2. If  $H'f > H_f'$ ,  $VD > VD'$ , that is, partial condensation occurs.

3. If  $H'f < H_f'$ ,  $VD < VD'$ , that is, a fresh quantity of vapour is required to maintain saturation. In this case the formula (1) can only be applied when we are sure that there is a sufficient excess of liquid to produce the fresh quantity of vapour which is required.

The general formulæ (1), (2), (3) furnish the solution of many particular problems which may be proposed by selecting some one of the variables for the unknown quantity.

**157. Aqueous Meteors.**—The name *meteor*, from the Greek *μετεώρος*, *aloft*, though more especially applied to the bright objects otherwise called shooting-stars and their like, likewise includes all the various phenomena which have their seat in the atmosphere; for example, clouds, rain, and lightning. This use of the word *meteor* is indeed somewhat rare; but the correlative term *meteorology* is invariably employed to denote the science which treats of these phenomena, in fact, the *science of matters pertaining to weather*.

By *aqueous meteors* are to be understood the phenomena which result from the condensation of aqueous vapour contained in the air, such as rain, dew, and fog. This condensation may occur in either of two ways. Sometimes it is caused by the presence of a cold body, which reduces the film of air in contact with it to a temperature below the dew-point, and thus produces the liquefaction or solidification of a portion of its vapour in the form of dew or hoarfrost.

When, on the contrary, the condensation of vapour takes place in the interior of a large mass of air, the resulting liquid or solid *falls* in obedience to gravity. This is the origin of rain and snow.

**158. Cloud and Mist.**—When vapour is condensed in the midst of the air, the first product is usually *mist* or *cloud*, a cloud being merely a mist at a great elevation in the air.

Natural clouds are similar in constitution to the cloudy substance which passes off from the surface of hot water, or which escapes in puffs from the chimney of a locomotive. In common language this substance is often called steam or vapour, but improperly, for steam

is, like air, transparent and invisible, and the appearance in question is produced by the presence of particles of liquid water, which have been formed from vapour by cooling it below its dew-point.

Different opinions have been put forward as to the nature of these particles, the difference having arisen in the attempt to explain their suspension in the atmosphere. Some have endeavoured to account for it by maintaining that they are hollow;<sup>1</sup> but even if we could conceive of any causes likely to lead to the formation of such bubbles, it would furnish no solution of the difficulty, for the air inclosed in a bubble is no rarer, but in fact denser, than the external air (see *Capillarity* in Part I); the bubble and its contents are therefore heavier than the air which it displaces.

It is more probable that the particles are solid spheres differing only in size from rain-drops. It has been urged against this view, that such drops ought to exhibit rainbows, and the objection must be allowed to have some weight. The answer to it is probably to be found in the excessive smallness of the globules. Indeed, the non-occurrence of bows may fairly be alleged as proving that the diameters of the drops are comparable with the lengths of waves of light.

This smallness of the particles is amply sufficient to explain all the observed facts of cloud suspension, without resorting to any special theory. It probably depends on the same principle as the suspension of the motes which are rendered visible when a beam of sunlight traverses a darkened room. It is true that these motes, which are small particles of matter of the most various kinds, are never seen resting stationary in the air; but neither are the particles which compose clouds. All who have ever found themselves in mountain mists must have observed the excessive mobility of their constituent parts, which yield to the least breath of wind, and are carried about by it like the finest dust. Sometimes, indeed, clouds have the appearance of being fixed in shape and position; but this is an illusion due to distance which renders small movements invisible. In many cases, the fixity is one of form and not of material; for example, the permanent cloud on a mountain-top often consists of successive portions of air, which become cloudy by condensation as they pass through the cold region at the top of the mountain, and recover their transparency as they pass away.

<sup>1</sup> Those who adopt this view call them *vesicles* (*vesica*, a bladder), and call mist or cloud vapour in the vesicular state.

**159. Varieties of Cloud.**—The cloud nomenclature generally adopted by meteorologists was devised by Howard, and is contained in his work on the climate of London. The fundamental forms, according to him, are three—*cirrus*, *cumulus*, and *stratus*.

1. *Cirrus* consists of fibrous, wispy, or feathery clouds, occupying the highest region of the atmosphere.



Fig. 96.—Cirrus.

The name *mare's-tails*, which is given them by sailors, describes their aspect well. They are higher than the greatest elevations attained by balloons, and are probably composed of particles of ice. It is in this species of cloud, and its derivatives,

that haloes are usually seen; and their observed forms and dimensions seem to agree with the supposition that they are formed by refractions and reflections from ice-crystals.

2. *Cumulus* consists of rounded masses, convex above and comparatively flat below. Their form bears a strong resemblance to heaps of cotton wool, hence the name *balls of cotton* and *wool-packs* applied to these clouds by sailors. They are especially prevalent in summer, and are probably formed by columns of ascending vapour which

become condensed at their upper extremities.

3. *Stratus* consists of horizontal sheets. Its situation is low in the atmosphere, and its formation is probably due to the cooling of the earth and the lower portion of the air by radiation. It is very frequently formed at sunset, and disappears at sunrise.

Of the intermediate forms it may suffice to mention *cirro-cumulus*, which floats at a higher level than cumulus, and consists usually of



Fig. 97.—Cumulus.

small roundish masses disposed with some degree of regularity. This is the cloud which forms what is known as a *mackerel sky*.

As a distinct form not included in Howard's classification, may be mentioned *scud*, the characteristic of which is that, from its low elevation, it *appears* to move with excessive rapidity.

Howard gives the name of *nimbus* to any cloud which is discharging rain; and, for no very obvious reason, he regards this rain-cloud as compounded of (or intermediate between) the three elementary types above defined.

The classification of clouds is a subject which scarcely admits of precise treatment; the varieties are so endless, and they shade so gradually into one another.

**160. Causes of the Formation of Cloud and Mist.**—Since clouds are merely condensed vapour, their formation is regulated by the causes which tend to convert vapour into liquid. Such liquefaction implies the presence of a quantity of vapour greater than that which, at the actual temperature, would be sufficient for saturation, a condition of things which may be brought about by the cooling of a mass of moist air in any of the following ways:—

- (1.) By radiation from the mass of air to the cold sky.
- (2.) By the neighbourhood of cold ground, for example, mountain-tops.
- (3.) By the cooling effect of expansion, when the mass of air ascends into regions of diminished pressure. This cooling of the ascending mass is accompanied by a corresponding warming of the air which

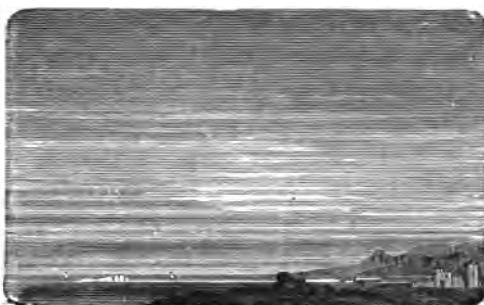


Fig. 98.—Stratus.



Fig. 99.—Nimbus.

descends—it may be in some distant locality—to supply its place.

Causes (2) and (3) combine to produce the excessive rainfall which generally characterizes mountainous districts.<sup>1</sup>

It is believed that waterspouts are produced by the rapid ascent of a stream of air up the axis of an aerial vortex.

(4) By the contact and mixture of cooler air.<sup>2</sup> It is obvious, however, that this cooler air must itself be warmed by the process; and as both the temperature and vapour-density of the mixture will be intermediate between those of the two components, it does not obviously follow (as is too often hastily assumed) that such contact tends to produce precipitation. Such is however the fact, and it depends upon the principle that the density of saturation increases faster as the temperature is higher; or, what is the same thing, that the curve in which temperature is the abscissa and maximum vapour-density the ordinate, is everywhere concave upwards.

It will be sufficient to consider the case of the mixing of two equal volumes of saturated air at different temperatures, which we will denote by  $t_1$  and  $t_2$ . Let the ordinates  $AA'$ ,  $BB'$  represent the densities of vapour for saturation at these temperatures,  $A'mB'$  being the intermediate portion of the curve, and  $Cm$  the ordinate at the middle point of  $AB$ , representing therefore the density of saturation for the temperature  $\frac{1}{2}(t_1+t_2)$ .

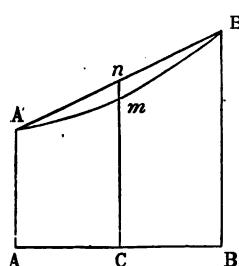


Fig. 100.

When the equal volumes are mixed, since the colder mass is slightly the greater, the temperature of the mixture will be something less than  $\frac{1}{2}(t_1+t_2)$ , and, if there were no condensation of vapour, the density of vapour in the mixture would be  $\frac{1}{2}(AA'+BB')=Cn$ . But the density for saturation is something less than  $Cm$ . The excess of vapour is therefore represented by something more than  $m n$ . The amount actually precipitated will, however, be less than this, since the portion which is condensed

<sup>1</sup> The rainiest place at present known in Great Britain is about a mile south of Steyning in Cumberland, where the annual rainfall is about 165 inches. The rainiest place in the world is believed to be Cherrapunji, in the Khasi Hills, about 300 miles N.E. of Calcutta, where the annual fall is about 610 inches.

<sup>2</sup> Contact with cooler air may be regarded as equivalent to mixing; for vapour diffuses readily.

gives out its latent heat, and thus contributes to keep up the temperature of the whole.

The cause here indicated combines with (3) to produce condensation when masses of air ascend.

On the surface of the earth mists are especially frequent in the morning and evening; in the latter case extending over all the surface; in the former principally over rivers and lakes. The mists of evening are due simply to the rapid cooling of the air after the heat of the sun has been withdrawn. In the morning another cause is at work. The great specific heat of water causes it to cool much more slowly than the air, so that the vapour rising from a body of water enters into a colder medium, and is there partly condensed, forming a mist, which, however, confines itself to the vicinity of the water, and is soon dissipated by the heat of the rising sun.

**161. Rain.**—In what we have stated regarding the constitution of clouds, it is implied that clouds are always raining, since the drops of which they are composed always tend to obey the action of gravity. But, inasmuch as there is usually a non-saturated region intervening between the clouds and the surface of the earth, these drops, when very small, are usually evaporated before they have time to reach the ground. Ordinary rain-drops are formed by the coalescing of a number of these smaller particles.

By the amount of annual rainfall at a given place is meant the depth of water that would be obtained if all the rain which falls there in a year were collected into one horizontal sheet; and the depth of rain that falls in any given shower is similarly reckoned. It is the depth of the pool which would be formed if the ground were perfectly horizontal, and none of the water could get away. The instrument employed for determining it is called a *rain-gauge*. It has various forms, one of which is represented in the adjoining figure. B is a funnel into which the rain falls, and from which it trickles into the reservoir A. It is drawn off by means of the stopcock r, and measured in a graduated glass.<sup>1</sup>



Fig. 101.  
Rain-gauge.

<sup>1</sup> The best work on the subject of rain and its measurement is Mr. Symons' little treatise [out of print] entitled *Rain*. Mr. Symons, who is at the head of an immense corps of volunteer observers of rain in all parts of the United Kingdom, also publishes an annual volume entitled *British Rainfall*.

The form recommended for use in ordinary localities by Mr. G. J. Symons the best authority on the subject, is called the Snowdon gauge, and is represented in Fig. 102. Its top is a cylinder with a sharp edge. A funnel is soldered to the inside of this cylinder at the distance of about one diameter from the top, and the neck of the funnel descends nearly to the bottom of a bottle which serves as

reservoir. A second cylinder, closed below and just large enough for the first to be slipped over it, contains the bottle, and is held in its place by four stakes driven into the ground. The upper cylinder with its attached funnel is slipped over the lower one, and pushed down till its further descent is stopped by the rim of the funnel meeting the edge of the lower cylinder.

The height of the receiving surface above the ground is 1 foot, and its diameter 5 inches. The graduated jar reads to hundredths of an inch, and measures up to half an inch. The bottle holds about 3 inches of rain, and in

the rare case of a fall exceeding that, the excess is saved by the lower cylinder.

Snow can be measured in either of the following ways:—

(1.) Melt what is caught in the gauge by adding to the snow a previously ascertained quantity of warm water, and then, after deducting this quantity from the total measurement, enter the residue as rain.

(2.) Select a place where the snow has not drifted, invert the upper cylinder with its attached funnel, and, turning it round, lift and melt what is inclosed.

It is essential that the receiving surface should be truly horizontal, otherwise the gauge will catch too much or too little according to the direction of the wind.

The best place for a rain-gauge is the centre of a level and open plot; and the height of its receiving surface should be not less than

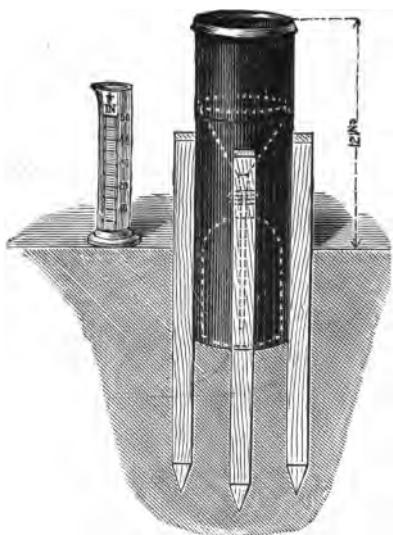


Fig. 102.—Snowdon Rain-gauge.

6 inches, to avoid in-splashing. The roof of a house is a bad place on account of the eddies which abound there.

A circumstance which has not yet been fully explained is that the higher a gauge is above the ground the less rain it catches. In the case of gauges on the top of poles in an open situation, the amount collected is diminished by  $\frac{1}{\sqrt{v}}$ th part of itself by doubling the height of the receiving surface, as shown by comparing gauges in the same plot of ground at heights ranging from 6 inches to 20 feet.<sup>1</sup>

By means of tipping-buckets and other arrangements, automatic records of rainfall are obtained at the principal observatories.

The mean annual rainfall, according to Mr. Symons, is 20 inches at Lincoln and Stamford; 21 at Aylesbury, Bedford, and Witham; 24 at London and Edinburgh; 30 at Dublin, Perth, and Salisbury; 33 at Exeter and Clifton; 35 to 36 at Liverpool and Manchester; 40 at Glasgow and Cork; 50 at Galway; 64 at Greenock and Inverary; 86 at Dartmoor; 91 on Benlomond; and upwards of 150 inches in some parts of the English lake district.

162. **Snow and Hail.**—Snow is probably formed by the direct passage of vapour into the solid state. Snow-flakes, when examined under the microscope, are always found to be made up of elements possessing hexagonal symmetry. In Fig. 103 are depicted various forms observed by Captain Scoresby during a long sojourn in the Arctic regions.

In these cold countries the air is often filled with small crystals of ice which give rise to the phenomena of haloes and parhelia.

Hail is probably due to the freezing of rain-drops in their passage through strata of air colder than those in which they were formed. Even in fine summer weather, a freezing temperature exists at the height of from 10,000 to 20,000 feet, and it is no unusual thing for a colder stratum to underlie a warmer, although, as a general rule, the temperature diminishes in ascending.

163. **Dew.**—By this name we denote those drops of water which are seen in the morning on the leaves of plants, and are especially noticeable in spring and autumn. We have already seen (§ 157) that dew does not fall, as it is not formed in the atmosphere, but in contact with the bodies on which it appears, being in fact due to their cooling after the sun has sunk below the horizon, when they lose heat by radiation to the sky. The lowering of temperature which thus occurs is much more marked for grass, stones, or bare earth than

<sup>1</sup> This appears from the table in Symons on *Rain*, p. 19.



Fig. 103.—Snow-crystals.

for the air, whose radiating power is considerably less. The consequence is a considerable difference of temperature between the surface of the ground and the air at the height of a few feet, a difference which is found by observation to amount sometimes to 8° or 10° C., and it is this which causes the deposition of dew. The surface of the earth, as it gradually cools, lowers the temperature of the adjacent air, which thus becomes saturated, and, on further cooling, yields up a portion of its vapour in the liquid form. If the temperature of the surface falls below 0° C., the dew is frozen, and takes the form of *hoar-frost*.

According to this theory, it would appear that the quantity of dew deposited upon a body should increase with the radiating power of its surface, and with its insulation from the earth or other bodies from which it might receive heat by conduction, both which conclusions are verified by observation.

The amount of deposition depends also in a great measure on the degree of exposure to the sky. If the body is partially screened, its radiation and consequent cooling are checked. This explains the practice which is common with gardeners of employing light coverings to protect plants from frost—coverings which would be utterly powerless as a protection against the cold of the surrounding air. The lightness of the dew on cloudy nights is owing to a similar cause; clouds, especially when overhead, acting as screens.

The deposition of dew is favoured by a slight motion of the atmosphere, which causes the lower strata of air to cool down more rapidly; but if the wind is very high, the different strata are so intermingled that very little of the air is cooled down to its dew-point, and the deposit is accordingly light. When these two obstacles are combined, namely a high wind and a cloudy sky, there is no dew at all.

## CHAPTER XII.

### CONDUCTION OF HEAT.

**164. Conduction.**—When heat is applied to one end of a bar of metal it is propagated through the substance of the bar, producing a rise of temperature which is first perceptible at near and afterwards at remote portions. This transmission of heat is called *conduction*. The best conductors are metals, but all bodies conduct heat more or less.

**165. Variable and Permanent Stages.**—Whenever heat is applied steadily to one end of a bar for a sufficient length of time, we may distinguish two stages in the experiment: 1st, the variable stage, during which all portions of the bar are rising in temperature; and, 2nd, the permanent state, which may subsist for any length of time without alteration. In the former stage the bar is gaining heat; that is, it is receiving more heat from the source than it gives out to surrounding bodies. In the latter stage the receipts and expenditure of heat are equal, and are equal not only for the bar as a whole, but for every small portion of which it is composed.

In this permanent state no further accumulation of heat takes place. All the heat which reaches an internal particle is transmitted by conduction, and the heat which reaches a superficial particle is given off partly by radiation and air-contact, and partly by conduction to colder neighbouring particles. In the earlier stage, on the contrary, only a portion of the heat received by a particle is thus disposed of, the remainder being accumulated in the particle, and serving to raise its temperature. Hence in this earlier stage the transmission of heat from the hot to the cold portions of the bar is checked by the absorption which goes on in the intervening parts. The amount of this absorption which occurs before the final condi-

tion is attained will depend upon the capacity of the substance for heat.

**166. Conductivity and Diffusivity.**—We may thus distinguish between two modes of estimating conducting power. What is especially understood as "conductivity" is independent of absorption, and therefore of thermal capacity. In order to obtain direct measures of it we must observe the flow of heat when the temperatures have become permanent. On the other hand "diffusivity" (to use the name introduced by Lord Kelvin) measures the *tendency to equalization of temperature*, which varies directly as conductivity, and inversely as the thermal capacity of unit volume of the body.

If we compare the times occupied by two equal and similar bodies in passing from the same initial distribution of temperature to the same final distribution, these times will be in the inverse ratio of the diffusivities. If the diffusivities are equal, the times will be the same, and in this case the quantities of heat gained or lost by corresponding portions of the two bodies are directly as the thermal capacities of equal volumes.<sup>1</sup>

**167. Definition of Conductivity.**—In order to give an accurate definition of conductivity, we must suppose a plate having one face at a uniform temperature  $v_1$ , and the other at a higher uniform temperature  $v_2$ , and we must suppose all parts of the plate to have attained their permanent temperatures. Then if  $x$  denote the thickness of the plate, and  $k$  the conductivity of the substance of which it is composed, the quantity,  $Q$ , of heat that flows through an area,  $A$ , of the plate in the time  $t$  will be

$$Q = kA \frac{v_2 - v_1}{x} t; \quad (1)$$

whence we have

$$k = \frac{Qx}{A(v_2 - v_1)t}; \quad (2)$$

and the conductivity may be defined as the quantity of heat that flows in unit time through unit area of a plate of unit thickness, with  $1^\circ$  of difference between the temperatures of its faces.

<sup>1</sup> The name *diffusivity* is employed by Lord Kelvin in the article "Heat" in the new edition of the *Encyclopaedia Britannica*. The name *thermometric conductivity* had previously been used in the same sense by Professor Clerk Maxwell, ordinary conductivity being called *thermal conductivity* for distinction. There is a close analogy between the conduction of heat and the diffusion of liquids; and the coefficient which expresses the facility with which one liquid diffuses into another is precisely analogous to "thermometric conductivity." Hence the name "diffusivity."

When the unit of heat employed in the reckoning is that which raises the temperature of unit volume of water by  $1^{\circ}$  (a unit which is practically the same as the gramme-degree), the conductivity  $k$  may be defined as the *thickness of a stratum of water* which would be raised  $1^{\circ}$  in temperature by the heat conducted in unit time through a plate of the substance of unit thickness having  $1^{\circ}$  of difference between its faces.

If for the words *thickness of a stratum of water* we substitute *thickness of a stratum of the substance*, we have the definition of *diffusivity*.

The thicknesses of the two strata will evidently be inversely as the thermal capacities of equal volumes. But the thermal capacity of unit volume of water is unity. Hence the "diffusivity" is equal to the "conductivity" divided by the thermal capacity of unit volume of the substance. If this thermal capacity be denoted by  $c$ , we have  $c = sd$ , where  $s$  denotes the specific heat (or thermal capacity of unit mass) and  $d$  the density (or mass of unit volume), and the diffusivity  $\kappa$  is

$$\kappa = \frac{k}{c} = \frac{k}{s d} \quad (3)$$

Strictly speaking,  $k$  in equations (1), (2) is the *mean conductivity* between the two temperatures  $v_1$ ,  $v_2$ , and the conductivity at any temperature  $v$  will be what  $k$  becomes when  $v_1$  and  $v_2$  are very nearly equal to each other and to  $v$ . The fact that conductivity varies with temperature was discovered by Forbes. He found that a specimen of iron which had a conductivity 207 at  $0^{\circ}$  C. had only a conductivity 124 at  $275^{\circ}$  C.

**168. Effect of Change of Units.**—In the C.G.S. (Centimetre-Gramme-Second) system, which we have explained in Part I., A is expressed in square centimetres,  $x$  in centimetres, and Q in gramme-degrees. It is immaterial whether the degree be Centigrade or Fahrenheit; for a change in the length of the degree will affect the numerical values of Q and of  $v_2 - v_1$  alike, and will leave the numerical value of  $\frac{Q}{v_2 - v_1}$ , and hence of  $\frac{Q x}{A (v_2 - v_1) t}$ , or  $k$  unaltered.

To find the effect of changes in the units of length and time, we must note that if the unit of length be  $x$  centimetres, the unit of area will be  $x^2$  square centimetres, and the unit of mass, being the mass of unit volume of cold water, will be  $x^3$  grammes. The new unit of heat will therefore be  $x^3$  gramme-degrees.

The new unit of conductivity will be the conductivity of a substance such that  $x^3$  gramme-degrees of heat flow in the new unit of time—which we will call  $t$  seconds—through  $x^2$  sq. cm. of a plate  $x$  cm. thick, with a difference of  $1^\circ$  between its faces. The conductivity of such a plate, when expressed in C.G.S. units, would be found by putting

$$Q = x^3, A = x^2, v_2 - v_1 = 1$$

in the formula

$$\frac{Q \cdot x}{A (v_2 - v_1) \cdot t}$$

and would be  $\frac{x^4}{x^2 t}$  or  $\frac{x^2}{t}$ .

Hence to reduce conductivities from the new scale to the C.G.S. scale we must multiply them by  $\frac{x^2}{t}$ ; and the same rule will apply to diffusivities, since the quantity  $c$  in equation (3) being the ratio of the thermal capacity of the substance to that of water, bulk for bulk, is independent of units.

**169. Illustrations of Conduction.**—The following experiments are often adduced in illustration of the different conducting and diffusing powers of different metals.

Two bars of the same size, but of different metals (Fig. 104), are placed end to end, and small wooden balls are attached by wax to

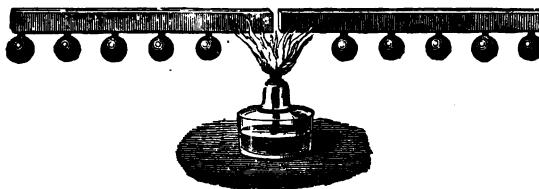


Fig. 104.—Balls Melted off.

their under surfaces at equal distances. The bars are then heated at their contiguous ends, and, as the heat extends along them, the balls successively drop off. If the conditions are in other respects equal, the balls will begin to drop off first from that which has the greater diffusivity, and the greatest number of balls will ultimately drop off from that which has the greater conductivity.

The well-known experiment of Ingenhousz (Fig. 105) is of the same kind. The apparatus consists of a box, with a row of holes in one of its sides, in which rods of different metals can be fixed. The rods having previously been coated with wax, the box is filled with

boiling water or boiling oil, which comes into contact with the inner ends of the rods. The wax gradually melts as the heat travels along the rods.

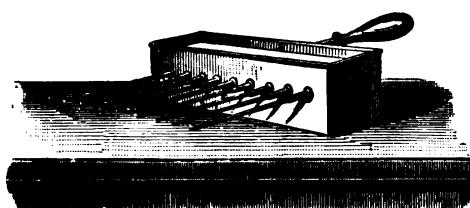


Fig. 105.—Ingenhousz's Apparatus.

The order in which the melting begins is the order of the diffusivities of the metals employed, and when it has reached its limit (if the temperature of the liquid be maintained constant) the order of the

lengths melted is the order of their conductivities.

**170. Metals the Best Conductors.**—Metals, though differing considerably one from another, are as a class greatly superior both in conductivity and diffusivity to other substances, such as wood, marble, brick. This explains several familiar phenomena. If the hand be placed upon a metal plate at the temperature of  $10^{\circ}$  C., or plunged into mercury at this temperature, a very marked sensation of cold is experienced. This sensation is less intense with a plate of marble at the same temperature, and still less with a piece of wood. The reason is that the hand, which is at a higher temperature than the substance to which it is applied, gives up a portion of its heat, which is conducted away by the substance, and consequently a larger portion of heat is parted with, and a more marked sensation of cold experienced, in the case of the body of greater conducting power.

**171. Davy Lamp.**—The conducting power of metals explains the curious property possessed by wire-gauze of cutting off a flame.

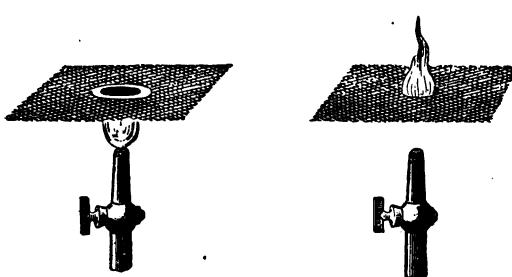


Fig. 106.—Action of Wire-gauze on Flame.

If, for example, a piece of wire-gauze be placed above a jet of gas, the flame is prevented from rising above the gauze. If the gas be first allowed to pass through the gauze, and then lighted above, the flame is cut off from

the burner, and is unable to extend itself to the under surface of the gauze. These facts depend upon the conducting power of

metallic gauze, in virtue of which the heat of the flame is rapidly dissipated at the points of contact, the result being a diminution of temperature sufficient to prevent ignition.

This property of metallic gauze has been turned to account for various purposes, but its most useful application is in the safety-lamp of Sir Humphry Davy.

It is well known that a gas called *fire-damp* is often given off in coal-mines. It is a compound of carbon and hydrogen, and is a large ingredient in ordinary coal-gas.

This fire-damp, when mixed with eight or ten times its volume of air, explodes with great violence on coming in contact with a lighted body. To obviate this danger, Davy invented the safety-lamp, which is an ordinary lamp with the flame inclosed by wire-gauze. The explosive gases pass through the gauze, and burn inside the lamp, in such a manner as to warn the miner of their presence; but the flame is unable to pass through the gauze.

**172. Walls of Houses.**—The knowledge of the relative conducting powers of different bodies has several important practical applications.

In cold countries, where the heat produced in the interior of a house should be as far as possible prevented from escaping, the walls should be of brick or wood, which have feeble conducting powers. If they are of stone, which is a better conductor, a greater thickness is required. Thick walls are also useful in hot countries in resisting the power of the solar rays during the heat of the day.



Fig. 107.—Davy Lamp.



Fig. 108.—Ice-house.

We have already alluded (§ 56) to the advantage of employing fire-brick, which is a bad conductor, as a lining for stoves.

The feeble conducting power of brick has led to its employment in the construction of ice-houses. These are round pits (Fig. 108), generally from 6 to 8 yards in diameter at top, and somewhat narrower at the bottom, where there is a grating to allow the escape of water. The inside is lined with brick, and the top is covered with straw, which, as we shall shortly see, is a bad conductor. In order to diminish as much as possible the extent of surface exposed to the



**Fig. 109.—Norwegian Cooking-box.**

action of the air, the separate pieces are dipped in water before depositing them in the ice-house, and, by their subsequent freezing together, a solid mass is produced, capable of remaining unmelted for a very long time.

**173. Norwegian Cooking-box.**—A curious application of the bad conducting power of felt is occasionally to be seen in the north of Europe in a kind of self-acting cooking-box. This is a box lined

inside with a thick layer of felt, into which fits a metallic dish with a cover. The dish is then covered with a cushion of felt, so as to be completely surrounded by a substance of very feeble conducting power. The method of employing the apparatus is as follows:—The meat which it is desired to cook is placed along with some water in the dish, the whole is boiled for a short time, and then transferred from the fire to the box, where the cooking is completed *without any further application of heat*. The resistance of the stuffing of the box to the escape of heat is exceedingly great; in fact, it may be shown that at the end of three hours the temperature of the water has fallen by only about  $10^{\circ}$  or  $15^{\circ}$  C. It has accordingly remained during all that time sufficiently high to conduct the operation of cooking.

**174. Experimental Determination of Conductivity.**—Several experimenters have investigated the conductivity of metals, by keeping one end of a metallic bar at a high temperature, and, after a sufficient lapse of time, observing the permanent temperatures assumed by different points in its length.

If the bar is so long that its further end is not sensibly warmer than the surrounding air, and if, moreover, Newton's law of cooling (§ 186) be assumed true for all parts of the surface, and all parts of a cross section be assumed to have the same temperature, the conductivity being also assumed to be independent of the temperature, it is easily shown that the temperatures of the bar at equidistant points in its length, beginning from the heated end, must exceed the atmospheric temperature by amounts forming a decreasing geometric series. Wiedemann and Franz, by the aid of the formula to which these assumptions lead,<sup>1</sup> computed the relative conducting powers of several of the metals, from experiments on thin bars, which were steadily heated at one end, the temperatures at various points in the length being determined by means of a thermo-electric junction clamped to the bar. The following were the results thus obtained:—

RELATIVE CONDUCTING POWERS.

Silver, . . . . .	100	Steel, . . . . .	12
Copper, . . . . .	77·6	Iron, . . . . .	11·9
Gold, . . . . .	53·2	Lead, . . . . .	8·5
Brass, . . . . .	33	Platinum, . . . . .	8·2
Zinc, . . . . .	19·9	Palladium, . . . . .	6·3
Tin, . . . . .	14·5	Bismuth, . . . . .	1·9

<sup>1</sup> See note B at the end of this chapter.

The *absolute* conductivity of wrought iron was investigated with great care by Principal Forbes, by a method which avoided some of the questionable assumptions above enumerated. The end of the bar was heated by a bath of melted lead kept at a uniform temperature, screens being interposed to protect the rest of the bar from the heat radiated by the bath. The temperatures at other points were observed by means of thermometers inserted in small holes drilled in the bar, and kept in metallic contact by fluid metal. In order to determine the loss of heat by radiation at different temperatures, a precisely similar bar, with a thermometer inserted in it, was raised to about the temperature of the bath, and the times of cooling down through different ranges were noted.

The conductivity of one of the two bars experimented on, varied from .01337 at 0° C. to .00801 at 275° C., and the corresponding numbers for the other bar were .00992 and .00724, the units being the foot, the minute, the degree (of any scale), and the foot-degree<sup>1</sup> (of the same scale). In both instances, the conductivity decreased regularly with increase of temperature.

To reduce these results to the C.G.S. scale, we must (as directed in § 168) multiply them by  $\frac{x^2}{t}$ , where  $x$  denotes the number of centimetres in a foot, or 30·48, and  $t$  the number of seconds in a minute;  $\frac{x^2}{t}$  will therefore be

$$\frac{(20\cdot48)^2}{60}, \text{ or } 15\cdot48.$$

The reduced values will therefore be as follows:—

	At 0°.	At 275°
1st bar,.....	.207 .....	.1240
2d bar,.....	.1536 .....	.1121

**175. Experimental Determination of Diffusivity.**—Absolute determinations of the diffusivity  $\kappa$  or  $\frac{k}{c}$  for the soil or rock at three localities in or near Edinburgh were made by Principal Forbes and Lord Kelvin. They were derived from observations on the temperature of the soil as indicated by thermometers having their bulbs buried at depths of 3, 6, 12 and 24 French feet. The annual range of temperature diminished rapidly as the depth increased, and this diminution of range was accompanied by a retardation of the times of maximum and minimum. The greater the diffusivity the more slowly will the range diminish and the less will be the retardation

<sup>1</sup> See § 60.

of phase. By a process described in note C at the end of this chapter the value of  $\kappa$  was deduced; and by combining this with the value of  $c$  (the product of specific heat and density), which was determined by Regnault, from laboratory experiments, the value of  $k$  or  $c\kappa$  was found. The following are the results, expressed in the C.G.S. scale:—

	$\frac{k}{c}$ or Diffusivity.	$\kappa$ or Conductivity.
Trap rock of Calton Hill, .....	.00786 .....	.00415
Sand of Experimental Garden,.....	.00872 .....	.00262
Sandstone of Craigleath Quarry,.....	.02311 .....	.01068

Similar observations made at Greenwich Observatory, and reduced by the editor of the present work, gave .01249 as the diffusivity of the gravel of Greenwich Observatory Hill.

A method based upon similar principles has since been employed by Ångström and also by Neumann for laboratory experiments; a bar of the substance under examination being subjected to regular periodical variations of temperature at one end, and the resulting periodic variations at other points in its length being observed. These gave the means of calculating the diffusivity, and then observations of the specific heat and density gave the conductivity. The following conductivities were thus obtained by Neumann:—

	Conductivity in C.G.S. units.
Copper,.....	1.108
Brass,.....	.302
Zinc,.....	.307
Iron,.....	.164
German silver,.....	.109

**176. Conductivity of Rocks.**—The following values of thermal and thermometric conductivity in C.G.S. units are averages based on the experiments of Professor Alexander Herschel.

	$k$ .	$\frac{k}{c}$
Granite,.....	.0053	.015
Limestone,.....	.005	.009
Sandstone, dry,.....	.0056	.012
Sandstone, thoroughly wet,.....	.0060	.010
Slate, along cleavage,.....	.0060	.010
Slate, across cleavage,.....	.0034	.006
Clay, sun-dried,.....	.0022	.0048
Red brick, .....	.0015	.0044
Plate-glass,.....	.0023	.0040

**177. Conducting Powers of Liquids.**—With the exception of mercury and other melted metals, liquids are exceedingly bad condc-

tors of heat. This can be shown by heating the upper part of a column of liquid, and observing the variations of temperature below. These will be found to be scarcely perceptible, and to be very slowly produced. If the heat were applied below (Fig. 110), we should have the process called *convection of heat*; the lower layers of liquid would rise to the surface, and be replaced by others which would rise in their turn, thus producing a circulation and a general heating of the liquid. On the other hand, when heat is applied above, the expanded

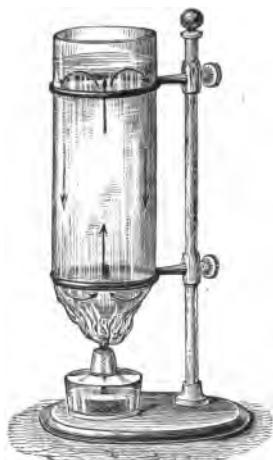


Fig. 110.—Liquid heated from below.



Fig. 111.—Boiling of Water over Ice.

layers remain in their place, and the rest of the liquid can be heated by conduction and radiation only.

The following experiment is one instance of the very feeble conducting power of water. A piece of ice is placed at the bottom of a glass tube (Fig. 111), which is then partly filled with water; heat is applied to the middle of the tube, and the upper portion of the water is readily raised to ebullition, without melting the ice below.

**178. Conducting Power of Water.**—The power of conducting heat possessed by water, though very small, is yet quite appreciable. This was established by Despretz by the following experiment. He took a cylinder of wood (Fig. 112) about a yard in height and eight inches in diameter, which was filled with water. In the side of this

cylinder were arranged twelve thermometers one above another, their bulbs being all in the same vertical through the middle of the liquid column. On the top of the liquid rested a metal box, which was filled with water at  $100^{\circ}$ , frequently renewed during the course of the experiment. Under these circumstances Despretz observed that the temperature of the thermometers rose gradually, and that a long time—about 30 hours—was required before the permanent state was

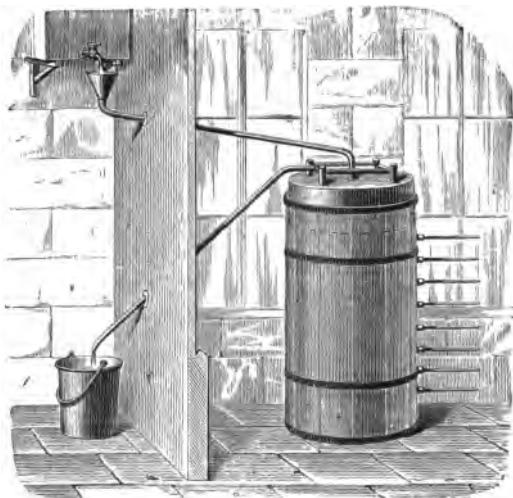


Fig. 112.—Despretz's Experiment.

assumed. Their permanent differences, which formed a decreasing geometric series, were very small, and were inappreciable after the sixth thermometer.

The increase of temperature indicated by the thermometers might be attributed to the heat received from the sides of the cylinder, though the feeble conducting power of wood renders this idea somewhat improbable. But Despretz observed that the temperature was higher in the axis of the cylinder than near the sides, which proves that the elevation of temperature was due to the passage of heat downwards through the liquid.

From experiments by Professor Guthrie,<sup>1</sup> it appears that water conducts better than any other liquid except mercury.

#### 179. Absolute Measurement of Conductivity of Water.—The abso-

<sup>1</sup> *B. A. Report*, 1868, and *Trans. R. S.* 1869.

lute value of  $k$  for water has been determined by Mr. J. T. Bottomley. Hot water was gently placed on the top of a mass of water nearly filling a cylindrical wooden vessel. Readings were taken from time to time of two horizontal thermometers, one of them a little lower than the other, which gave the difference of temperature between the two sides of the intervening stratum. The quantity of heat conducted in a given time through this stratum was known from the rise of temperature of the whole mass of water below, as indicated by an upright thermometer with an exceedingly long cylindrical bulb extending downwards from the centre of the stratum in question nearly to the bottom of the vessel. A fourth thermometer, at the level of the bottom of the long bulb, showed when the increase of temperature had extended to this depth, and as soon as this occurred (which was not till an hour had elapsed) the experiment was stopped.

The result of these experiments is that the value of  $k$  for water is from .0020 to .0023, which is nearly identical with its value for ice, this latter element, as determined by Professor George Forbes, being .00223.

The conductivity of water seems to be much greater than that of wood.

**180. Conducting Power of Gases.**—Of the conducting powers of gases it is almost impossible to obtain any direct proofs, since it is exceedingly difficult to prevent the interference of convection and direct radiation. However, we know at least that they are exceedingly bad conductors. In fact, in all cases where gases are inclosed in small cavities where their movement is difficult, the system thus formed is a very bad conductor of heat. This is the cause of the feeble conducting powers of many kinds of cloth, of fur, eider-down, felt, straw, saw-dust, &c. Materials of this kind, when used as articles of clothing, are commonly said to be *warm*, because they hinder the heat of the body from escaping. If a garment of eider-down or fur were compressed so as to expel the greater part of the air, and to reduce the substance to a thin sheet, it would be found to be a much less warm covering than before, having become a better conductor. We thus see that it is the presence of air which gives these substances their feeble conducting power, and we are accordingly justified in assuming that air is a bad conductor of heat.

**181. Conductivity of Hydrogen.**—The conducting power of hydrogen is much superior to that of the other gases—a fact which agrees

with the view entertained by chemists, that this gas is the vapour of a metal. The good conductivity of hydrogen is shown by the following experiments:—

1. Within a glass tube (Fig. 113) is stretched a thin platinum wire, which is raised to incandescence by the passage of an electric current. When air, or any gas other than hydrogen, is passed through the tube, the incandescence continues, though with less vividness than in vacuo; but it disappears as soon as hydrogen is employed.

2. A thermometer is placed at the bottom of a vertical tube, and heated by a vessel containing boiling water which is placed at the top of the tube. The tube is exhausted of air, and different gases are successively admitted. In each case the indication of the thermometer is found to be lower than for vacuum, except when the gas is hydrogen. With this gas, the difference is in the opposite direction, showing that the diminution of radiation has been more than compensated by the conducting power of the hydrogen.

**NOTE A. DIFFERENTIAL EQUATION FOR LINEAR FLOW OF HEAT.**—The mode of obtaining differential equations for the variation of temperature at each point of a body during the variable stage, may be illustrated by considering the simplest case, that in which the isothermal surfaces (surfaces of equal temperature) are parallel planes, and therefore the lines of flow (which must always be normal to the isothermal surfaces) are parallel straight lines.

Let  $x$  denote distance measured in the direction in which heat is flowing,  $v$  the temperature at the time  $t$  at a point specified by  $x$ ,  $k$  the conductivity, and  $c$  the thermal capacity per unit volume (both at the temperature  $v$ ). Then the flow of heat per unit time past a cross section of area  $A$  is  $-kA \frac{dv}{dx}$ , and the flow past an equal and parallel section further on by the small distance  $\delta x$  is greater by the amount

$$A \frac{d}{dx} \left( -k \frac{dv}{dx} \right) \delta x.$$



Fig. 113.—Cooling by Contact of Hydrogen.

This latter expression therefore represents the loss of heat from the intervening prism  $A \delta x$ , and the resulting fall of temperature is the quotient of the loss by the thermal capacity  $c A \delta x$ , which quotient is

$$\frac{1}{c} \frac{d}{dx} \left( -k \frac{dv}{dx} \right).$$

This, then, is the fall of temperature per unit time, or is  $-\frac{dv}{dt}$ . If the variation of  $k$  is insensible, so that  $\frac{dk}{dx}$  can be neglected, the equation becomes

$$\frac{dv}{dt} = \frac{k}{c} \frac{d^2 v}{dx^2},$$

which applies approximately to the variations of temperature in the soil near the surface of the earth,  $x$  being in this case measured vertically. For the integral of this equation, see Note C.

**NOTE B. FLOW OF HEAT IN A BAR** (§ 174).—If  $p$  and  $s$  denote the perimeter and section of the bar,  $k$  the conductivity, and  $h$  the coefficient of emission of the surface at the temperature  $v$ , the heat emitted in unit time from the length  $\delta x$  is  $hvp\delta x$ , if we assume as our zero of temperature the temperature of the surrounding air. But the heat which passes a section is  $-sk \frac{dv}{dx}$ , and that which passes a section further on by the amount  $\delta x$  is less by the amount  $sk \frac{d^2 v}{dx^2} \delta x$ ; and this difference must equal the amount emitted from the intervening portion of the surface. Hence we have the equation  $\frac{d^2 v}{dx^2} = \frac{hp}{ks} v$ , the integral of which for the case supposed is

$$v = V e^{-x \sqrt{\frac{hp}{ks}}}$$

$V$  denoting the temperature at the heated end.

**NOTE C. DEDUCTION OF DIFFUSIVITY FROM OBSERVATIONS OF UNDERGROUND TEMPERATURE** (§ 175).—Denoting the diffusivity  $\frac{k}{c}$  by  $\kappa$ , the equation of Note A is

$$\frac{dv}{dt} = \kappa \frac{d^2 v}{dx^2}. \quad (4)$$

This equation is satisfied by

$$v = e^{-\alpha x} \sin (\beta t - \alpha x), \quad (5)$$

where  $\alpha$  and  $\beta$  are any two constants connected by the relation

$$\frac{\beta}{2\alpha^2} = \kappa; \quad (6)$$

for we find, by actual differentiation,

$$\begin{aligned} \frac{dv}{dx} &= e^{-\alpha x} \{ -\alpha \sin (\beta t - \alpha x) - \alpha \cos (\beta t - \alpha x) \}; \\ \frac{d^2 v}{dx^2} &= e^{-\alpha x} \{ \alpha^2 \sin (\beta t - \alpha x) + \alpha^2 \cos (\beta t - \alpha x) + \alpha^2 \cos (\beta t - \alpha x) - \alpha^2 \sin (\beta t - \alpha x) \} \\ &= e^{-\alpha x} 2\alpha^2 \cos (\beta t - \alpha x); \\ \frac{dv}{dt} &= e^{-\alpha x} \beta \cos (\beta t - \alpha x) = \frac{\beta}{2\alpha^2} \frac{d^2 v}{dx^2}. \end{aligned}$$

More generally, equation (4) will be satisfied by making  $v$  equal to the sum of any

number of terms similar to the right-hand member of (5), each multiplied by any constant, and a constant term may be added. In fact we may have

$$\begin{aligned} v = A_0 + A_1 e^{-a_1 x} \sin(\beta_1 t - a_1 x + E_1) + A_2 e^{-a_2 x} \sin(\beta_2 t - a_2 x + E_2) \\ + A_3 e^{-a_3 x} \sin(\beta_3 t - a_3 x + E_3) + \text{&c.,} \end{aligned} \quad (7)$$

where  $A_0, A_1, E_1, \text{ &c.}$ , are any constants.

Let  $x$  be measured vertically downwards from the surface of the ground (supposed horizontal); then at the surface the above expression becomes

$$v = A_0 + A_1 \sin(\beta_1 t + E_1) + A_2 \sin(\beta_2 t + E_2) + A_3 \sin(\beta_3 t + E_3) + \text{&c.} \quad (8)$$

Now, if  $T$  denote a year, it is known that the average temperature of the surface at any time of year can be expressed, in terms of  $t$  the time reckoned from 1st of January or any stated day, by the following series:—

$$v = A_0 + A_1 \sin\left(\frac{2\pi t}{T} + E_1\right) + A_2 \sin\left(\frac{4\pi t}{T} + E_2\right) + A_3 \sin\left(\frac{6\pi t}{T} + E_3\right) + \text{&c.,} \quad (9)$$

where  $A_0$  is the mean temperature of the whole year, and  $A_1, A_2, A_3, \text{ &c.}$ , which are called the *amplitudes* of the successive terms, diminish rapidly. The term which contains  $A_1$  and  $E_1$  (called the annual term), completes its cycle of values in a year, the next term in half a year, the next in a third of a year, and so on. The annual term is much larger, and more regular in its values from year to year than any of those which follow it. Each term affords two separate determinations of the diffusivity. Thus, for the annual term, we have, by comparing (8) and (9)—

$$\beta_1 = \frac{2\pi}{T}, \text{ whence, by (8),}$$

$$a_1 = \sqrt{\frac{\beta_1}{2\kappa}} = \sqrt{\frac{\pi}{T\kappa}}.$$

At the depth  $x$ , the amplitude of this term will be

$$A_1 e^{-a_1 x},$$

the logarithm of which is

$$\log A_1 - a_1 x.$$

Hence  $a_1$  can be deduced from a comparison of the annual term at two different depths, by dividing the difference of the Napierian logarithms of the amplitudes by the difference of depth.

But  $a_1$  can also be determined by comparing the values of  $\beta_1 t - a_1 x + E_1$  at two depths for the same value of  $t$ , and taking their difference (which is called the *retardation of phase*, since it expresses how much later the maximum, minimum, and other phases, occur at the lower depth than at the upper). This difference, divided by the difference of depth, will be equal to  $a_1$ .

These two determinations of  $a_1$  ought to agree closely, and  $\kappa$  will then be found by the equation

$$a_1 = \sqrt{\frac{\pi}{T\kappa}}.$$

## CHAPTER XIII.

### RADIATION.

**182. Radiation distinct from Conduction.**—When two bodies at different temperatures are placed opposite to each other, with nothing between them but air or some other transparent medium, the hotter body gives heat to the colder by *radiation*. It is by radiation that the earth receives heat from the sun and gives out heat to the sky; and it is by radiation that a fire gives heat to a person sitting in front of it.

Radiation is broadly distinguished from conduction. In conduction, the transmission of heat is effected by the warming of the intervening medium, each portion of which tends to raise the succeeding portion to its own temperature.

On the other hand heat transmitted from one body to another by radiation does not affect the temperature of the intervening medium. The heat which we receive from the sun has traversed the cold upper regions of the air; and paper can be ignited in the focus of a lens of ice, though the temperature of ice cannot exceed the freezing-point.

Conduction is a gradual, radiation an instantaneous process. A screen interposed between two bodies instantly cuts off radiation between them; and on the removal of such a screen radiation instantly attains its full effect. Radiant heat, in fact, travels with the velocity of light, and it is subject to laws similar to the laws of light; for example, it is usually propagated only in straight lines.

Strictly speaking, radiant heat, like latent heat, is not heat at all, but is a form of energy which is readily converted into heat. Its nature is precisely the same as that of light, the difference between them being only a difference of degree, as will be more fully explained in treating of the analysis of light by the prism and spectro-

scope. The present chapter will contain numerous instances of the analogy between the properties of non-luminous radiant heat and well-known characteristics of light.

**183. A Ponderable Medium not Essential.**—The transmission of the sun's heat to the earth shows that radiation is independent of any ponderable medium. But since the solar heat is accompanied by light, it might still be questioned whether dark heat could be propagated through a vacuum.

This was tested by Rumford in the following way:—He constructed a barometer (Fig. 114), the upper part of which was expanded into a globe, and contained a thermometer hermetically sealed into a hole at the top of the globe, so that the bulb of the thermometer was at the centre of the globe. The globe was thus a Torricillian vacuum-chamber. By melting the tube with a blow-pipe, the globe was separated, and was then immersed in a vessel containing hot water, when the thermometer was immediately observed to rise to a temperature evidently higher than could be due to the conduction of heat through the stem. The heat had therefore been communicated by direct radiation through the vacuum between the sides of the globe and the bulb *a* of the thermometer.

**184. Radiant Heat travels in Straight Lines.**—In a uniform medium the radiation of heat takes place in straight lines. If, for instance, between a thermometer and a source of heat, there be placed a number of screens, each pierced with a hole, and if the screens be so arranged that a straight line can be drawn without interruption from the source to the thermometer, the temperature of the latter immediately rises; if a different arrangement be adopted, the heat is stopped by the screens, and the thermometer indicates no effect.

Hence we can speak of *rays* of heat just as we speak of rays of light. Thus we say that rays of heat issue from all points of the surface of a heated body, or that such a body emits rays of heat. The word *ray* when thus used scarcely admits of precise definition. It is a popular rather than a scientific term; for no finite quantity of heat or light can travel along a mathematical line. In a mere



Fig. 114.—Rumford's Experiment.

geometrical sense the rays are the lines which indicate the direction of propagation.

It is now generally admitted that both heat and light are due to a vibratory motion which is transmitted through space by means of a fluid called ether. According to this theory the rays of light and heat are lines drawn in all directions from the origin of motion, and along which the vibratory movement advances.

**185. Surface Conduction.**—The cooling of a hot body exposed to the air is effected partly by radiation, and partly by the conduction of heat from the surface of the body to the air in contact with it. The activity of the surface-conduction is greatly quickened by wind, which brings continually fresh portions of cold air into contact with the surface, in the place of those which have been heated.

The cooling of a body *in vacuo* is effected purely by radiation, except in so far as there may be conduction through its supports.

**186. Newton's Law of Cooling.**—In both cases, if the body be exposed in a chamber of uniform temperature, the rate at which it loses heat is approximately proportional to the excess of the temperature of its surface above that of the chamber, and the proportionality is sensibly exact when the excess does not exceed a few degrees. If the body be of sensibly uniform temperature throughout its whole mass, as in the case of a thin copper vessel full of water which is kept stirred, its fall of temperature is proportional to its loss of heat, and hence the rate at which its temperature falls is proportional to the excess of its temperature above that of the chamber. Practically if the body be a good conductor and of small dimensions—say a copper ball an inch in diameter, or an ordinary mercurial thermometer—the fall of its temperature is nearly in accordance with this law, which is called *Newton's law of cooling*. The observed fact is that when the readings of the thermometer are taken at equal intervals of time, their excesses above the temperature of the inclosure (which is kept constant) form a diminishing geometrical progression.

To show that this is equivalent to Newton's law, let  $\theta$  denote the excess of temperature at time  $t$ ; then, in the notation of the differential calculus,  $-\frac{d\theta}{dt}$  is the rate of cooling; and Newton's law asserts that this is proportional to  $\theta$ , or that

$$-\frac{d\theta}{dt} = A\theta, \quad (1)$$

where A is a constant multiplier. This is equivalent to

$$-\frac{d\theta}{\theta} = A dt, \quad (2)$$

which asserts that for equal small intervals of time the differences between the temperatures are proportional to the temperatures. But if the differences between the successive terms of a series are proportional to the terms themselves, the series is geometrical; for if we have

$$\frac{\theta_1 - \theta_2}{\theta_1} = \frac{\theta_2 - \theta_3}{\theta_2} = \frac{\theta_3 - \theta_4}{\theta_3},$$

we obtain, by subtracting unity from each member,

$$\frac{\theta_2}{\theta_1} = \frac{\theta_3}{\theta_2} = \frac{\theta_4}{\theta_3};$$

that is,  $\theta_1, \theta_2, \theta_3, \theta_4$  are in geometrical progression.

The expression  $-\frac{d\theta}{\theta}$  in equation (2) is, by the rules of the differential calculus, equal to  $-d \log \theta$ ; hence equation (2) shows that  $\log \theta$  diminishes by equal amounts in equal times. Log  $\theta$  here denotes the Napierian logarithm of  $\theta$ ; and since common logarithms are equal to Napierian logarithms multiplied by a constant factor, the common logarithm of  $\theta$  will also diminish by equal amounts in equal times. The constant A in equation (1) or (2) will be determined from the experimental results by dividing the decrement of  $\log \theta$  by the interval of time.

We have been assuming that the body is hotter than the chamber or inclosure; but a precisely similar law holds for the warming of a body which is colder than the inclosure in which it is placed.

**187. Dulong and Petit's Law of Cooling.**—Newton's law is sensibly accurate for *small* differences of temperature between the body and the inclosure. Dulong and Petit conducted experiments on the cooling of a thermometer by radiation in vacuo with excesses of temperature varying from  $20^\circ$  to  $240^\circ$  C., from which they deduced the formula

$$-\frac{d\theta}{dt} = c a^v (a^\theta - 1);$$

or, as it may be otherwise written,

$$-\frac{d\theta}{dt} = c(a^{v+\theta} - a^v),$$

where  $v$  denotes the temperature of the walls of the inclosure, which was preserved constant during each experiment,  $v + \theta$  the temperature of the thermometer, and  $-\frac{d\theta}{dt}$  the rate of cooling. The other letters,  $c$  and  $a$ , denote constants. When the temperatures are Centi-

grade, the constant  $a$  is 1·0077; when they are Fahrenheit it is 1·0043, the form of the expression for the rate of cooling being unaffected by a change of the zero from which temperatures are reckoned. The value of  $c$  depends upon the size of the bulb and some other circumstances, and is changed by a change of zero.

**188. Consequences of this Law.**—The formula in its first form shows that, for the same excess  $\theta$ , the cooling is more rapid at high than at low temperatures.

Employing the Centigrade scale, we have  $a=1\cdot0077$ , whence  $\log a=0\cdot0077$  nearly, and since

$$\theta^2 = 1 + \theta \log a + \frac{1}{2}(\theta \log a)^2 + \frac{1}{3}(\theta \log a)^3 + \text{ &c.},$$

Dulong and Petit's formula, in its first form, gives

$$-\frac{d\theta}{dt} = c(1\cdot0077)^v \{0\cdot0077 \theta + \frac{1}{2}(0\cdot0077 \theta)^2 + \text{ &c.}\},$$

which shows that, for a given temperature of the inclosure, the rate of cooling is not strictly proportional to  $\theta$ , but is equal to  $\theta$  multiplied by a factor which increases with  $\theta$ , this factor being proportional to  $1 + \frac{1}{2}(0\cdot0077 \theta) + \frac{1}{3}(0\cdot0077 \theta)^2 + \text{ &c.}$

When  $\theta$  is small enough for  $0\cdot0077 \theta$  to be neglected in comparison with unity, the factor will be sensibly constant, in accordance with Newton's law.

**189. Theory of Exchanges.**—The second form of Dulong and Petit's formula, namely

$$-\frac{d\theta}{dt} = c(a^{v+\theta} - a^v),$$

suggests that an unequal *exchange* of heat takes place between the thermometer and the walls, the thermometer giving to the walls a quantity of heat  $ca^{v+\theta}$  (where  $v+\theta$  denotes the temperature of the thermometer), and the walls giving to the thermometer the smaller quantity  $ca^v$ .

This is the view now commonly adopted with respect to radiation in general. It has been fully developed by Professor Balfour Stewart under the name of the *theory of exchanges*. Its original promulgator, Prévost of Geneva, called it the theory of *mobile equilibrium of temperature*.

The theory asserts that all bodies are constantly giving out radiant heat, at a rate depending upon their substance and temperature, but independent of the substance or temperature of the bodies which surround them; and that when a body is kept at a uniform temperature, it receives back just as much heat as it gives out.

According to this view, two bodies at the same temperature, exposed to mutual radiation, exchange equal amounts of heat; but if two bodies have unequal temperatures, that which is at the higher temperature gives to the other more than it receives in exchange.<sup>1</sup>

**190. Law of Inverse Squares.**—If we take a delicate thermometer and place it at successively increasing distances from a source of heat, the temperature indicated by the instrument will exceed that of the atmosphere by decreasing amounts, showing that the intensity of radiant heat diminishes as the distance increases. The law of variation may be discovered by experiment. In fact, when the excess of temperature of the thermometer becomes fixed, we know that the heat received is equal to that lost by radiation; but this latter is, by Newton's law, proportional to the excess of temperature above that of the surrounding air; we may accordingly consider this excess as the measure of the heat received. It has been found, by experiments at different distances,<sup>2</sup> that the excess is inversely proportional to the square of the distance; we may therefore conclude that *the intensity of the heat received from any source of heat varies inversely as the square of the distance*.

The following experiment, devised by Tyndall, supplies another simple proof of this fundamental law:—

The thermometer employed is a Melloni's pile, the nature of which we shall explain in § 197. This is placed at the small end of a hollow cone, blackened inside, so as to prevent any reflection of heat from its inner surface. The pile is placed at S and S' in front of a vessel filled with boiling water, and coated with lamp-black on the side next the pile. It will now be observed that the temperature indicated by the pile remains constant for all distances. This result proves the law of inverse squares. For the arrangement adopted prevents the pile from receiving more heat than that due to the area of A B in the first case, and to the area A' B' in the second. These are the areas of two circles, whose radii are respectively proportional to S O and S' O; and the areas are consequently proportional to the squares of S O and S' C. Since, therefore, these two areas communi-

<sup>1</sup> For a full account of this subject see "Report on the Theory of Exchanges," by Balfour Stewart, in *British Association Report*, 1861, p. 97; and *Stewart on Heat*, book ii. chap. iii.

<sup>2</sup> The dimensions of the source of heat must be small in comparison with the distance of the thermometer, as otherwise the distances of different parts of the source of heat from the thermometer are sensibly different. In this case, the amount of heat received varies directly as the solid angle subtended by the source of heat.

cate the same quantity of heat to the pile, the intensity of radiation must vary inversely as the squares of the distances S O and S' O.

The law of inverse squares may also be established *a priori* in the following manner:—

Suppose a sphere of given radius to be described about a radiating particle as centre. The total heat emitted by the particle will be received by the sphere, and all points on the sphere will experience

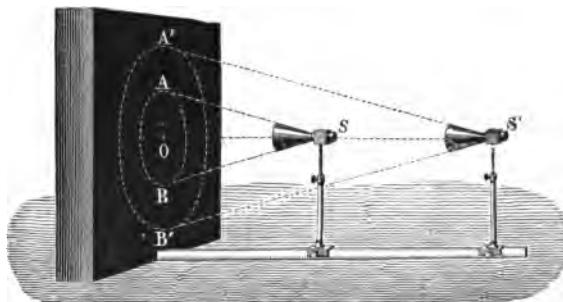


Fig. 115.—Law of Inverse Squares.

the same calorific effect. If now the radius of the sphere be doubled, the surface will be quadrupled, but the total amount of heat remains the same as before, namely, that emitted by the radiating particle. Hence we conclude that the quantity of heat absorbed by a given area on the surface of the large sphere is one-fourth of that absorbed by an equal area on the small sphere; which agrees with the law stated above.

This demonstration is valid, whether we suppose the radiation of heat to consist in the emission of matter or in the emission of energy; for energy as well as matter is indestructible, and remains unaltered in amount during its propagation through space.

**191. Law of the Reflection of Heat.**—When a ray of heat strikes a polished surface, it is reflected according to the same law as a ray of light.

**192. Burning Mirrors.**—All rays, either of heat or light, falling on a parabolic mirror in directions parallel to its axis (AC, Fig. 116) are reflected accurately to its focus F, and all rays from F falling on the mirror are reflected parallel to the axis. A spherical concave mirror is a small portion of a sphere, and rays parallel to its axis are reflected so as approximately to pass through its “principal focus” F (same figure), which is midway between A, the central point of the mirror, and C, the centre of the sphere.

When the axis of a concave mirror, of either form, is directed towards the sun, intense heat is produced at the focus, especially if

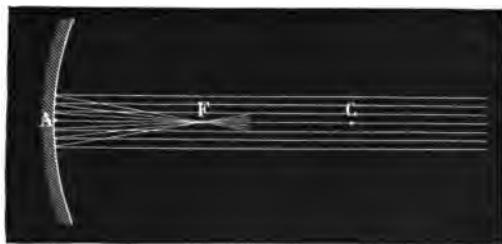


Fig. 116.—Focus of Concave Mirror.

the mirror be large. Fig. 117 represents such a mirror suitably mounted for producing ignition of combustible substances. Tschirnhausen's mirror, which was constructed in 1687, and was about  $6\frac{1}{2}$  feet in diameter, was able to melt copper or silver, and to vitrify brick. Instead of curved mirrors, Buffon employed a number of movable plane mirrors, which were arranged so that the different pencils of heat-rays reflected by them converged to nearly the same point. In this way he obtained an extremely powerful effect, and was able, for instance, to set wood on fire at a distance of between 80 and 90 yards. This is the method which Archimedes is said to have employed for the destruction of the Roman fleet in the siege of Syracuse; and though the truth of the story is considered doubtful, it is not altogether absurd.



Fig. 117.—Burning Mirror.

**193. Conjugate Mirrors.**—Fig. 118 represents an experiment which is said to have been first performed by Pictet of Geneva.

Two large parabolic mirrors are placed facing each other, at any convenient distance, with their axes in the same straight line. In

the focus of one of them is placed a small furnace, or a red-hot cannon-ball, and in the focus of the other some highly inflammable material, such as phosphorus or gun-cotton. On exciting the furnace with bellows, the substance in the other focus immediately takes fire. With two mirrors of 14 inches diameter, gun-cotton may thus be set on fire at a distance of more than 30 feet. The explanation is very easy. The rays of heat coming from the focus of the first

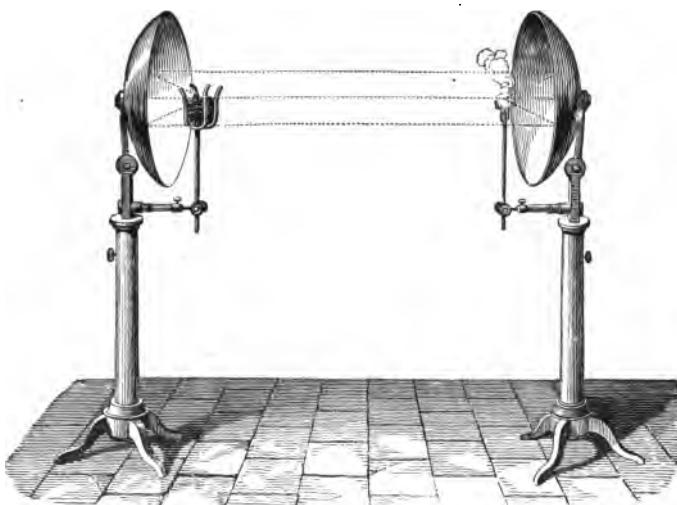


Fig. 118.—Conjugate Mirrors.

mirror are reflected in parallel lines, and, on impinging upon the surface of the second mirror, converge again to its focus, and are thus concentrated upon the inflammable material placed there.

Careful adjustment is necessary to the success of the experiment, and the adjustment is most easily made by first placing a source of light (such as the flame of a candle) in one focus, and forming a luminous image of it in the other. We have thus a convincing proof that heat and light obey the same law as regards direction of reflection.

**194. Reflection, Diffusion, Absorption, and Transmission.**—When radiant heat is incident upon the surface of a body it is divided into several distinct parts. A portion is *regularly reflected* according to the law given above. A portion is *irregularly* or *diffusely reflected* and is scattered through space in all directions. A portion penetrates into the body so as to be *absorbed* by it, and to contribute to

raise its temperature; and in some cases a fourth portion passes through the body without contributing to raise its temperature. This portion is said to be *transmitted*.

**195. Coefficient of Absorption and Coefficient of Emission.**—Applying Newton's law (§ 186), let  $\theta$  be the small difference of temperature between the surface of the body and the inclosure, and  $S$  the area of this surface, which we suppose to have no concavities, then the quantity of heat gained or lost by the body per unit of time is expressed by the formula

$$AS\theta,$$

where  $A$  is a constant depending on the nature of the body and more especially on the nature of its surface. This constant  $A$  may be called indifferently the *coefficient of emission* or the *coefficient of absorption*, inasmuch as it has the same value (the temperature of the body being given) whether the inclosure be colder or warmer than the body. Experiments conducted by Mr. M'Farlane under the direction of Lord Kelvin, showed that when the surface of the body (a copper ball) and the walls of the inclosure were both covered with lamp-black, the inclosure being full of air at atmospheric pressure, the value of the coefficient  $A$  in C.G.S. units is about  $\frac{1}{1000}$ , that is to say  $\frac{1}{1000}$  of a gramme-degree of heat is gained or lost per second for each square centimetre of surface of the body, when there is  $1^{\circ}$  of difference between its temperature and that of the walls of the inclosure. When the surface of the body (the copper ball) was polished, the walls of the inclosure being blackened as before, the coefficient had only  $\frac{1}{10}$  of its former value. It was estimated that of the value  $\frac{1}{1000}$  for blackened surfaces, one-half is due to atmospheric contact and the other half to radiation. As the excess of temperature of the body above that of the walls increased from  $5^{\circ}$  to  $60^{\circ}$ , the quantity of heat emitted, instead of being increased only twelve-fold, was increased about sixteen-fold for the blackened and fifteen-fold for the polished ball.

When air is excluded, and the gain or loss of heat is due to pure radiation between the body and the walls, the coefficient  $A$  represents, according to the theory of exchanges, the difference between the absolute emission at the temperature of the body and at a temperature  $1^{\circ}$  higher or lower.

**196. Limit to Radiating Power.**—It is obviously impossible for a body to absorb more radiant heat than falls upon it. There must,

therefore, be a limiting value of  $A$  applicable to a body which would absorb all the heat that falls upon it and not absorb or transmit any. Such a body would possess perfect emissive power for radiant heat. Hence it appears that good radiation depends rather upon defect of resistance than upon any positive power. A perfect radiator would be a substance whose surface offered no resistance to the passage of radiant heat in either direction; while an imperfect radiator is one whose surface allows a portion to be communicated through it, and reflects another portion regularly or irregularly.

The reflecting and diffusive powers of lamp-black are so insignificant, at temperatures below  $100^{\circ}$ , that this substance is commonly adopted as the type of a perfect radiator, and the emissive and absorptive powers of other substances are usually expressed by comparison with it.

## CHAPTER XIV.

### RADIATION (CONTINUED).

197. Thermoscopic Apparatus employed in researches connected with Radiant Heat.—An indispensable requisite for the successful study of radiant heat is an exceedingly delicate thermometer. For this purpose Leslie, about the beginning of the present century, invented the differential thermometer, with which he conducted some very important investigations, the main results of which are still acknowledged to be correct. Modern investigators, as Melloni, Laprovostaye, &c., have exclusively employed Nobili's thermo-multiplier, which is an instrument of much greater delicacy than the differential thermometer.

The thermo-pile, invented by Nobili, and improved by Melloni, consists essentially of a chain (Fig. 119) formed of alternate elements of bismuth and antimony. If the ends of the chain be connected by a wire, and the alternate joints slightly heated, a thermo-electric current will be produced, as will be explained hereafter. The amount of current increases with the number of elements, and with the difference of temperatures of the opposite junctions.

In the pile as improved by Melloni, the elements are arranged side by side so as to form a square bundle (Fig. 120), whose opposite ends consist of the alternate junctions. The whole is contained in a copper case, with covers at the two ends, which can be removed when it is desired to expose the faces of the pile to the action of heat. Two metallic rods connect the terminals of the thermo-electric series



Fig. 119.—Nobili's Thermo-electric Series.

with wires leading to a galvanometer,<sup>1</sup> so that the existence of any current will immediately be indicated by the deflection of the needle. The amounts of current which correspond to different deflections are known from a table compiled by a method which we shall explain hereafter. Consequently, when a beam of radiant heat strikes the pile, an electric current is produced, and the amount of this current

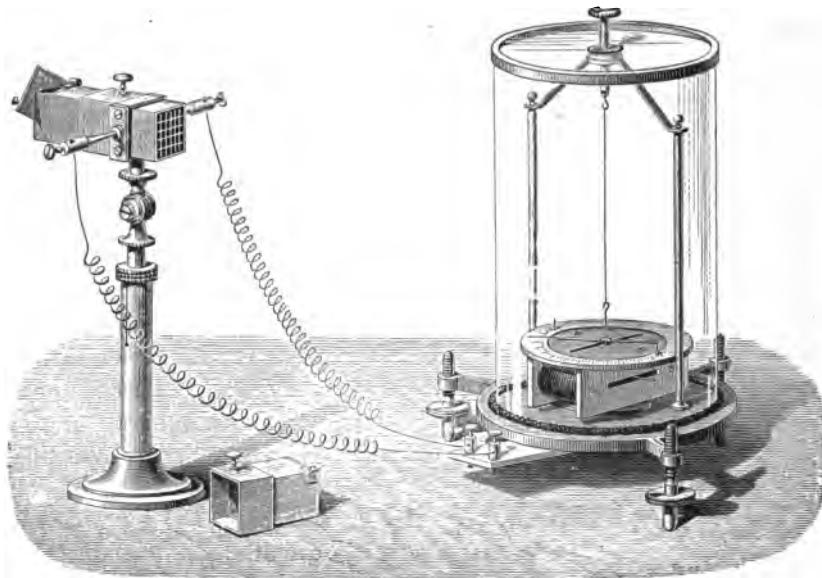


Fig. 120.—Melloni's Thermo-multiplier.

is given by the galvanometer. We shall see hereafter, when we come to treat of thermo-electric currents, that within certain limits, which are never exceeded in investigations upon radiant heat, the current is proportional to the difference of temperature between the two ends of the pile. As soon as all parts of the pile have acquired their permanent temperatures, the quantity of heat received during any interval of time from the source of heat will be equal to that lost to the air and surrounding objects. But this latter is, by Newton's law, proportional to the excess of temperature above the surrounding air, and therefore to the difference of temperature between the two ends of the pile. The current is therefore proportional to the quantity of heat received by the instrument. We have thus in Nobili's pile a thermometer of great delicacy, and admirably adapted

<sup>1</sup>The pile and galvanometer together constitute the thermo-multiplier.

to the study of radiant heat; in fact, the immense progress which has been made in this department of physics is mainly owing to this invention of Nobili.

**198. Measurement of Emissive Powers.**—The following arrangement was adopted by Melloni for the comparison of emissive powers. A graduated horizontal bar (Fig. 121) carries a cube, the different sides of which are covered with different substances. This is filled with water, which is maintained at the boiling-point by means of a spirit-lamp placed beneath. The pile is placed at a convenient distance,

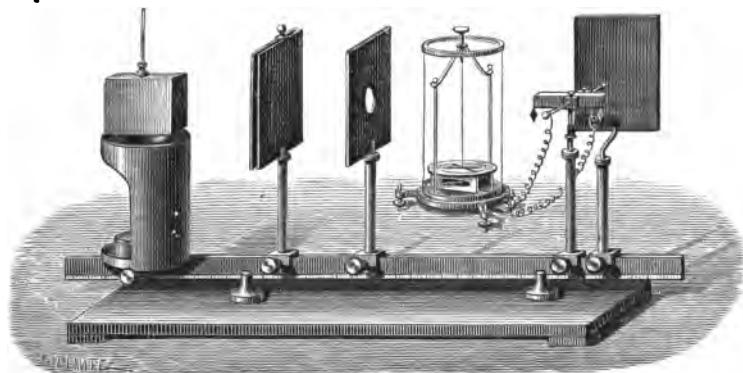


Fig. 121.—Measurement of Emissive Powers.

and the radiation can be intercepted at pleasure by screens arranged for the purpose. The whole forms what is called Melloni's apparatus.

If we now subject the pile to the heat radiated from each of the faces in turn, we shall obtain currents proportional to the emissive powers of the substances with which the different faces are coated.

From a number of experiments of this kind it has been found that lamp-black has the greatest radiating power of all known substances, while the metals are the worst radiators. Some of the most important results are given in the following table, in which the emissive powers of the several substances are compared with that of lamp-black, which is denoted by 100:—

RELATIVE EMISSIVE POWERS AT 100° C.

Lamp-black, . . . . .	100	Steel, . . . . .	17
White-lead, . . . . .	100	Platinum, . . . . .	17
Paper, . . . . .	98	Polished brass, . . . . .	7
Glass, . . . . .	90	Copper, . . . . .	7
Indian ink, . . . . .	85	Polished gold, . . . . .	3
Shellac, . . . . .	72	Polished silver, . . . . .	3

By modified arrangements of the same apparatus, he measured the absorbing, reflecting, diffusing, and transmitting powers of different substances, and established the fact that all those powers vary according to the source from which the incident radiation is derived.

For example when the source was a hot-water cube, lamp-black and white-lead showed equal absorptions; but when it was the flame of an oil lamp, the absorbing power of white-lead was only 53 per cent of that of lamp-black.

The upshot of the matter is that radiant heat exhibits differences precisely analogous to the different colours of light—a fact which Melloni expressed by the name *thermochroë* or heat-colour. A hot-water cube or other non-luminous source emits only long waves; and as the temperature of the source rises, shorter waves are added, till some of the waves are so short as to come within the limits of visibility, and the body is then said to be *incandescent*. Waves of radiant heat, when short enough to produce the sensation of vision, are called waves of light, and there is no difference between radiant heat and light except a difference of wave-length.

**199. Diathermancy.**—The fact that radiant heat from non-luminous sources could be transmitted through certain transparent substances was established by Pictet of Geneva; and Prévost confirmed the fact by showing that such transmission could occur even through a sheet of ice. Substances which transmit radiant heat are called *diathermanous*. Diathermancy is merely transparency to rays of long wave-length.

Rock-salt is noted for its diathermancy. Even when dirty-looking, it is much more transparent to dark rays than the clearest glass. Alum, on the other hand, is noted for its opacity to dark rays, and quartz (rock crystal) for its transparency to ultra-violet rays.

Tyndall has shown that a solution of iodine in bisulphide of carbon, though excessively opaque to light, allows heat to pass in large quantity. He raised platinum foil to incandescence by placing it in the focus of the mirror of an electric lamp whose light was stopped by interposing a rock-salt trough containing this solution. To this transformation of dark radiant heat into light he gave the name of *calorescence*.

**200. Selective Emission and Absorption.**—In order to connect together the various phenomena which may be classed under the general title of selective radiation and absorption, it is necessary to

form some such hypothesis as the following. The atoms or molecules of which any particular substance is composed, must be supposed to be capable of vibrating freely in certain periods, which, in the case of gases, are sharply defined, so that a gas is like a musical string, which will vibrate in unison with certain definite notes and with no intermediate ones. The particles of a solid or liquid, on the other hand, are capable of executing vibrations of any period lying between certain limits; so that they may perhaps be compared to the body of a violin, or to the sounding-board of a piano; and these limits (or at all events the upper limit) alter with the temperature, so as to include shorter periods of vibration as the temperature rises.

These vibrations of the particles of a body are capable of being excited by vibrations of like period in the external ether, in which case the body absorbs radiant heat. But they may also be excited by the internal heat of the body; for whenever the molecules experience violent shocks, which excite tremors in them, these are the vibrations which they tend to assume. In this case the particles of the body excite vibrations of like period in the surrounding ether, and the body is said to emit radiant heat.

One consequence of these principles is that a diathermanous body is particularly opaque to its own radiation. Rock-salt transmits 92 per cent of the radiation from most sources of heat; but if the source of heat be another piece of rock-salt, especially if it be a thin plate, the amount transmitted is much less, a considerable proportion being absorbed. The heat emitted and absorbed by rock-salt is of exceedingly low refrangibility.

Glass largely absorbs heat of long period, such as is emitted by bodies whose temperatures are not sufficiently high to render them luminous, but allows rays of shorter period, such as compose the luminous portion of the radiation from a lamp-flame, to pass almost entire. Accordingly glass when heated emits a copious radiation of non-luminous heat, but comparatively little light.

Experiment shows that if various bodies, whether opaque or transparent, colourless or coloured, are heated to incandescence in the interior of a furnace, or of an ordinary coal-fire, they will all, while in the furnace, exhibit the same tint, namely the tint of the glowing coals. In the case of coloured transparent bodies, this implies that the rays which their colour prevents them from transmitting from the coals behind them are radiated by the bodies themselves most

copiously; for example, a glass coloured red by oxide of copper permits only red rays to pass through it, absorbing all the rest, but it does not show its colour in the furnace, because its own heat causes it to radiate just those rays which it has the power of absorbing, so that the total radiation which it sends to the eye of a spectator, consisting partly of the radiation due to its own heat, and partly of rays which it transmits from the glowing fuel behind it, is exactly the same in kind and amount as that which comes direct from the other parts of the fire. This explanation is verified by the fact that such glass, if heated to a high temperature in a dark room, glows with a green light.

A plate of tourmaline cut parallel to the axis has the property of breaking up the rays of heat and light which fall upon it into two equal parts, which exhibit opposite properties as regards polarization. One of these portions is very largely absorbed, while the other is transmitted almost entire. When such a plate is heated to incandescence, it is found to radiate just that description of heat and light which it previously absorbed; and if it is heated in a furnace, no traces of polarization can be detected in the light which comes from it, because the transmitted and emitted light exactly complement each other, and thus compose ordinary or unpolarized light.

Spectrum analysis as applied to gases furnishes perhaps still more striking illustrations of the equality of selective radiation and absorption. The radiation from a flame coloured by vapour of sodium—for example, the flame of a spirit-lamp with common salt sprinkled on the wick—consists mainly of vibrations of a definite period, corresponding to a particular shade of yellow. When vapour of sodium is interposed between the eye and a bright light yielding a continuous spectrum, it stops that portion of the light which corresponds to this particular period, and thus produces a dark line in the yellow portion of the spectrum.

An immense number of dark lines exist in the spectrum of the sun's light, and no doubt is now entertained that they indicate the presence, in the outer and less luminous portion of the sun's atmosphere, of gaseous substances which vibrate in periods corresponding to the position of these lines in the spectrum.

201. Our knowledge of solar radiation has been greatly extended in recent years by the researches of Professor Langley of the Smithsonian Institution, conducted by means of an instrument of his own invention called the *bolometer*, which is more sensitive than a

thermopile. The instrument contains an exceedingly fine platinum wire, which is placed successively in different portions of the spectrum, and any change in the temperature of this wire, however slight, is immediately revealed by the deflection of a galvanometer, the wire being, in fact, one of the two arms of a "Wheatstone's Bridge" (§ 209, Part III.).

In order to avoid the absorption of some of the sun's rays which necessarily occurs in transmission through lenses and prisms, he availed himself of the concave "gratings" recently invented by Rowland (§ 271, Part IV.), which produce a spectrum without the aid of a lens.

He has thus been able to trace the ultra-red portion of the solar spectrum much further than it was ever traced before. The wave-length of the extreme violet, in terms of the unit generally employed, being about 3900, and that of the extreme red about 7600, he has traced the ultra-red as far as wave-length 28,000.

By comparing observations made at different heights, some of them being at an elevation of 13,000 feet, on Mount Whitney in Southern California, he has shown that the atmosphere is more transparent to these ultra-red rays than to any others, and that all through the spectrum the absorption is in some inverse ratio to the wave-length. The notion, which has been entertained by many competent authorities, that the atmosphere acts like the glass of a green-house and keeps the earth warm by its opacity to long waves, must, therefore, be discarded, at all events for such climates as those of Pennsylvania and Southern California.

## CHAPTER XV.

### THERMO-DYNAMICS.

**202. Connection between Heat and Work.**—That heat can be made to produce work is evident when we consider that the work done by steam-engines and other heat-engines is due to this source.

Conversely, by means of work we can produce heat. Fig. 122 represents an apparatus called the fire-syringe or pneumatic tinder-box, consisting of a piston working tightly in a glass barrel. If a piece of cotton wool moistened with bisulphide of carbon be fixed in the cavity of the piston, and the air be then suddenly compressed, so much heat will be developed as to produce a visible flash of light.

A singular explanation of this effect was at one time put forward. It was maintained that heat or *caloric* was a kind of imponderable fluid, which, when introduced into a body, produced at once an increase of volume and an elevation of temperature. If, then, the body was compressed, the caloric which had served to dilate it was, so to speak, *squeezed out*,<sup>1</sup> and hence the development of heat. An immediate consequence of this theory is that heat cannot be increased or diminished in quantity, but that any addition to the quantity of heat in one part of a system must be compensated by a corresponding loss in another part. But we know that there are cases in which heat is produced by two bodies in contact, without our being able to observe any traces of this compensating process. An instance of this is the production of heat by friction.



Fig. 122.  
Fire-syringe.

<sup>1</sup> In other words, the thermal capacity of the body was supposed to be diminished, so that the amount of heat contained in it, without undergoing any increase, was able to raise it to a higher temperature.

**203. Heat produced by Friction.**—Friction is a well-known source of heat. Savages are said to obtain fire by rubbing two pieces of dry wood together. The friction between the wheel and axle in railway-carriages frequently produces the same effect, when they have been insufficiently greased; and the stoppage of a train by applying a brake to the wheels usually produces a shower of sparks.

The production of heat by friction may be readily exemplified by the following experiment, due to Tyndall. A glass tube containing water (Fig. 123) and closed by a cork, can be rotated rapidly about

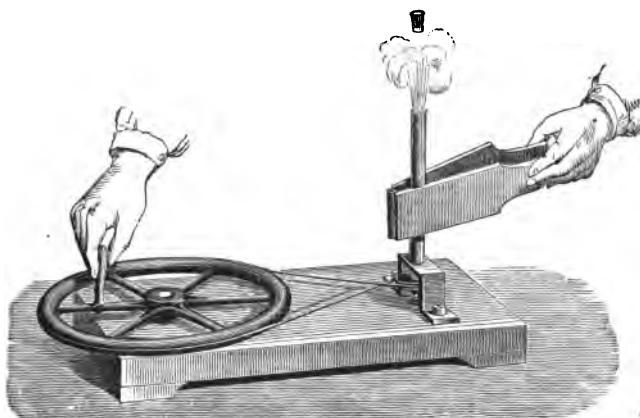


Fig. 123.—Heat produced by Friction.

its axis. While thus rotating, it is pressed by two pieces of wood, covered with leather. The water is gradually warmed, and finally enters into ebullition, when the cork is driven out, followed by a jet of steam. Friction, then, may produce an intense heating of the bodies rubbed together, without any corresponding loss of heat elsewhere.

At the close of last century, Count Rumford (an American in the service of the Bavarian government) called attention to the enormous amount of heat generated in the boring of cannon, and found, in a special experiment, that a cylinder of gun-metal was raised from the temperature of 60° F. to that of 130° F. by the friction of a blunt steel borer, during the abrasion of a weight of metal equal to about  $\frac{1}{950}$  of the whole mass of the cylinder. In another experiment, he surrounded the gun by water (which was prevented from entering the

bore), and, by continuing the operation of boring for  $2\frac{1}{2}$  hours, he made this water boil. In reasoning from these experiments, he strenuously maintained that heat cannot be a material substance, but must consist in motion.

The advocates of the caloric theory endeavoured to account for these effects by asserting that caloric, which was latent in the metal when united in one solid mass, had been forced out and rendered sensible by the process of disintegration under heavy pressure. This supposition was entirely gratuitous, no difference having ever been detected between the thermal properties of entire and of comminuted metal; and, to account for the observed effect, the latent heat thus supposed to be rendered sensible in the abrasion of a given weight of metal, must be sufficient to raise  $950 \times 70$ , that is 66,500 times its own weight of metal through  $1^{\circ}$ .

Yet, strange to say, the caloric theory survived this exposure of its weakness, and the, if possible, still more conclusive experiment of Sir Humphry Davy, who showed that two pieces of ice, when rubbed together, were converted into water, a change which involves not the evolution but the absorption of latent heat, and which cannot be explained by diminution of thermal capacity, since the specific heat of water is much greater than that of ice.

Davy, like Rumford, maintained that heat consisted in motion, and the same view was maintained by Dr. Thos. Young; but the doctrine of caloric nevertheless continued to be generally adopted until about the year 1840, since which time, the experiments of Joule, the eloquent advocacy of Mayer, and the mathematical deductions of Thomson, Rankine, and Clausius, have completely established the mechanical theory of heat, and built up an accurate science of thermodynamics.

**204. Foucault's Experiment.**—The relations existing between electrical and thermal phenomena had considerable influence in leading to correct views regarding the nature of heat. An experiment devised by Foucault illustrates these relations, and at the same time furnishes a fresh example of the production of heat by the performance of mechanical work.

The apparatus consists (Fig. 124) of a copper disc which can be made to rotate with great rapidity by means of a system of toothed wheels. The motion is so free that a very slight force is sufficient to maintain it. The disc rotates between two pieces of iron, constituting the armatures of one of those temporary magnets which are obtained

by the passage of an electric current (called electro-magnets). If, while the disc is turning, the current is made to pass, the armatures become strongly magnetized, and a peculiar action takes place between them and the disc, consisting in the formation of induced currents in the latter, accompanied by a resistance to motion. As

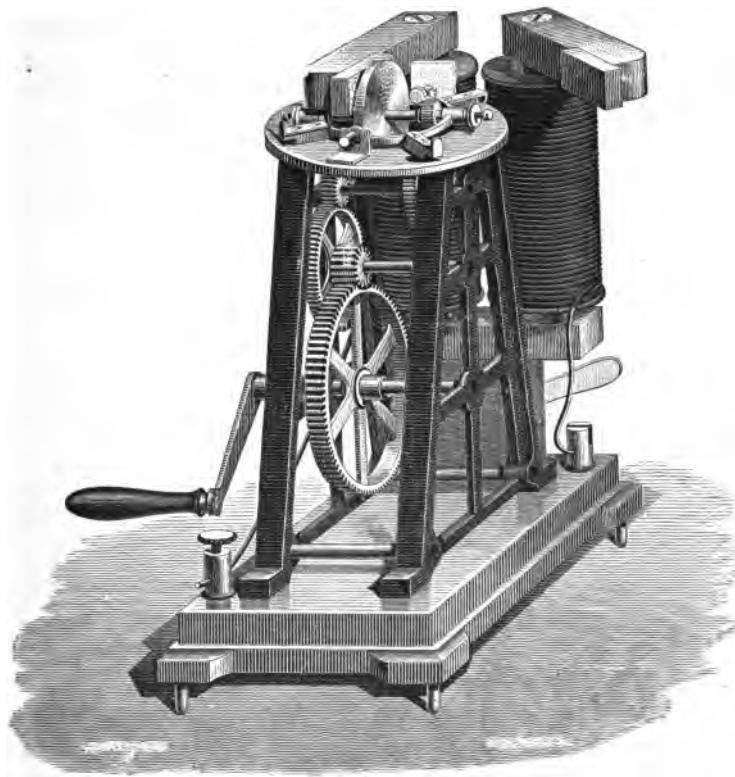


Fig. 124.—Foucault's Apparatus.

long as the magnetization is continued, a considerable effort is necessary to maintain the rotation of the disc; and if the rotation be continued for two or three minutes, the disc will be found to have risen some  $50^{\circ}$  or  $60^{\circ}$  C. in temperature, the heat thus acquired by the disc being the equivalent of the work done in maintaining the motion. It is to be understood that, in this experiment, the rotating disc does not touch the armatures; the resistance which it experiences is due entirely to invisible agencies.

The experiment may be varied by setting the disc in very rapid rotation, while no current is passing, then leaving it to itself, and immediately afterwards causing the current to pass. The result will be, that the disc will be brought to rest almost instantaneously, and will undergo a very slight elevation of temperature, the heat gained being the equivalent of the motion which is destroyed.

**205. Mechanical Equivalent of Heat.**—The first precise determination of the numerical relation subsisting between heat and mechanical work was obtained by the following experiment of Joule. He constructed an agitator which is somewhat imperfectly represented in Fig. 125, consisting of a vertical shaft carrying several sets of paddles revolving between stationary vanes, these latter serving to

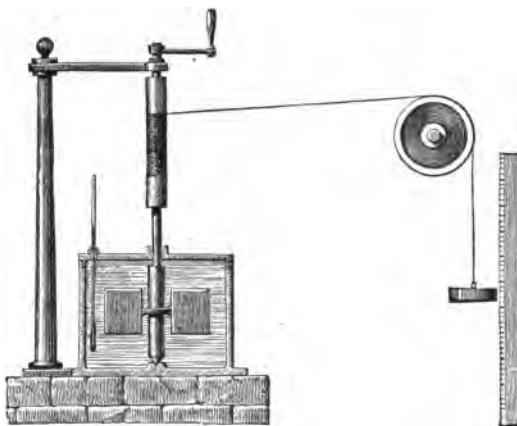


Fig. 125.—Determination of the Mechanical Equivalent of Heat.

prevent the liquid in the vessel from being bodily whirled in the direction of rotation. The vessel was filled with water, and the agitator was made to revolve by means of a cord, wound round the upper part of the shaft, carried over a pulley, and attached to a weight, which by its descent drove the agitator, and furnished a measure of the work done. The pulley was mounted on friction-wheels, and the weight could be wound up without moving the paddles. When all corrections had been applied, it was found that the heat communicated to the water by the agitation amounted to one pound-degree Fahrenheit for every 772 foot-pounds of work spent in producing it. This result was verified by various other forms of experiment, and is certainly very near the truth.

For an elevation of  $1^{\circ}$  Centigrade, the corresponding number will be  $772 \times 9/5$ , that is, 1390.

For an elevation of  $1^{\circ}$  C. in a kilogramme of water, the number of kilogrammetres of work required will be the number of metres in 1390 feet, that is, 424. Any one of these numbers is called a value of *Joule's equivalent*, and is usually denoted by the symbol J. It is sometimes called the *mechanical equivalent of heat*, or more fully, the *mechanical equivalent of the unit of heat*.

**206. Rowland's Determination.**—Among subsequent verifications of Joule's result, the experiments of Professor Rowland<sup>1</sup> at Baltimore are specially important. He drove, by means of a steam-engine, a revolving stirrer, having numerous blades pierced with holes and passing between similar blades fixed to the water-vessel. The revolutions were counted by means of an endless screw on the shaft of the stirrer; and the mutual couple between the stirrer and the vessel was determined by measuring the counterbalancing couple which prevented the vessel from turning; this counterbalancing couple consisting of (1) a pair of equal weights acting (by means of pulleys) on the circumference of a horizontal wheel and composing a couple of any constant magnitude; (2) the torsion of a suspending wire, which, by increasing or diminishing with the couple to be equilibrated, made the arrangement stable. The average elevation of temperature in each trial was about  $20^{\circ}$ , whereas in Joule's classical experiment it was only a fraction of a degree.

Rowland's result, for water at  $10^{\circ}$  C., was 428·5, when expressed in kilogrammetres at Baltimore, which is equivalent to 428·0 kilogrammetres at Manchester, where Joule's determination was made. Eliminating the local element of gravitation by reducing to absolute measure, his result for water at  $10^{\circ}$  C. was *42 millions of ergs for  $1^{\circ}$  C. of change of temperature in a gramme of water*, temperature being reckoned on the absolute thermo-dynamic scale which will be explained further on in this chapter. At  $5^{\circ}$  C. the number (instead of 42) was 42·12; at  $15^{\circ}$  C., 41·89; at  $20^{\circ}$  C., 41·79; at  $30^{\circ}$  C., 41·71; and at  $35^{\circ}$  C., 41·73; showing that the specific heat of water passes through a minimum at about  $30^{\circ}$  C.

42 million ergs may conveniently be adopted as the value of Joule's equivalent in the C.G.S. system.

**207. First Law of Thermo-dynamics.**—Whenever work is per-

<sup>1</sup> Rowland on the *Mechanical Equivalent of Heat*. Cambridge (U.S.) University Press, 1880.

formed by the agency of heat, an amount of heat disappears equivalent to the work performed; and whenever mechanical work is spent in generating heat, the heat generated is equivalent to the work thus spent; that is to say, we have in both cases

$$W = JH;$$

$W$  denoting the work,  $H$  the heat, and  $J$  Joule's equivalent. This is called the *first law of thermo-dynamics*, and it is a particular case of the great natural law which asserts that energy may be transmuted, but is never created or destroyed.

It may be well to remark here that work is not energy, but is rather the process by which energy is transmuted, amount of work being measured by the amount of energy transmuted. Whenever work is done, it leaves an effect behind it in the shape of energy of some kind or other, equal in amount to the energy consumed in performing the work, or, in other words, equal to the work itself.

As regards the nature of heat, there can be little doubt that heat properly so called, that is, sensible as distinguished from latent heat, consists in some kind of motion, and that quantity of heat is quantity of energy of motion, or kinetic energy, whereas latent heat consists in energy of position or potential energy.

We have already had in the experiments of Rumford, Davy, Foucault, and Joule, some examples of transmutation of energy; but it will be instructive to consider some additional instances.

When a steam-engine is employed in hauling up coals from a pit, an amount of heat is destroyed in the engine equivalent to the energy of position which is gained by the coal.

In the propulsion of a steam-boat with uniform velocity, or in the drawing of a railway train with uniform velocity on a level, there is no gain of potential energy, neither is there, as far as the vessel or train is concerned, any gain of kinetic energy. In the case of the steamer, the immediate effect consists chiefly in the agitation of the water, which involves the generation of kinetic energy; and the ultimate effect of this is a warming of the water, as in Joule's experiment. In the case of the train, the work done in maintaining the motion is spent in friction and concussions, both of which operations give heat as the ultimate effect. Here, then, we have two instances in which heat, after going through various transformations, reappears as heat at a lower temperature.

In starting a train on a level the heat destroyed in the engine

finds its equivalent mainly in the energy of motion gained by the train; and this energy can again be transformed into heat by turning off the steam and applying brakes to the wheels.

When a cannon-ball is fired against an armour plate, it is heated red-hot if it fails to penetrate the plate, the energy of the moving ball being in this case obviously converted into heat. If the plate is penetrated, and the ball lodges in the wooden backing, or in a bank of earth, the ball will not be so much heated, although the total amount of heat generated must still be equivalent to the energy of motion destroyed. The ruptured materials, in fact, receive a large portion of the heat. The heat produced in the rupture of iron is well illustrated by punching and planing machines, the pieces of iron punched out of a plate, or the shavings planed off it, being so hot that they can scarcely be touched, although the movements of the punch and plane are exceedingly slow. The heat gained by the iron is, in fact, the equivalent of the work performed, and this work is considerable on account of the great force required.

**208. Heat of Compression and Cold of Expansion.**—The heating of a gas by compression or its cooling by expansion is nearly the same in amount as if a quantity of heat equivalent to the work of compression or expansion were given to or taken from the gas at constant volume. This approximate equality was established by an experiment of Joule's. He immersed two equal vessels in water, one of them containing highly-compressed air, and the other being vacuous; and when they were both at the temperature of the water he opened a stop-cock which placed the vessels in communication. The compressed air thus expanded to double its volume, but no change could be detected in the temperature of the surrounding water. The work of expansion produced its equivalent, first in kinetic energy *plus* friction, and finally in heat; and this heat sensibly compensated the cooling effect of the expansion.

Subsequent experiments by Thomson and Joule showed that the cooling effect slightly predominates; hence, conversely, the heating effect of compression slightly exceeds the equivalent of the work done in compressing the gas. The excess of the cooling effect amounted to .26 of a degree Centigrade in the case of air, when the difference between the initial and final pressures was 1 atmosphere, and to .26n when the difference was n atmospheres.

The mode of experimenting consisted in steadily forcing air through a plug of cotton wool, and comparing the temperatures of

the entering and the issuing air. The friction of the air in passing through the plug generates heat, which in the long run is imparted to the air as it flows through; and this warming effect is combined with the cooling effect of expansion. The cooling effect preponderated, not only in the case of air but in the case of every gas that was tried except hydrogen, which showed a slight rise of temperature. For carbonic acid at about 10° C. the fall of temperature was about 4½ times as great as for air.

**209. Work in Expansion.**—The work done by a gas in expanding against uniform hydrostatic or pneumatic pressure may be computed by *multiplying the increase of volume by the pressure per unit area*. For, if we suppose the expanding body to be immersed in an incompressible fluid without weight, confined in a cylinder by means of a movable piston under constant pressure, the work done by the expanding body will be spent in driving back the piston. Let  $A$  be the area of the piston,  $x$  the distance it is pushed back, and  $p$  the pressure per unit area. Then the increment of volume is  $Ax$ , and the work done is the product of the force  $pA$  by the distance  $x$ , which is the same as the product of  $p$  by  $Ax$ .

**210. Difference of the two Specific Heats.**—Let a gramme of air, occupying a volume  $V$  cub. cm. at the absolute temperature  $T$ °, be raised at the constant pressure of  $P$  grammes per sq. cm. to the temperature  $T + 1$ °. It will expand by the amount  $\frac{V}{T}$ , and will do work to the amount  $\frac{VP}{T}$  in pushing back the surrounding resistances. Now the value of  $\frac{VP}{T}$  is (§ 50) the same for all pressures and temperatures. But at 0° C. and 760 mm. we have  $T = 273$ ,  $P = 1033$ , and since the volume of 1·293 grammes is 1 litre or 1000 cub. cm., we have

$$V = \frac{1000}{1.293},$$

and

$$\frac{VP}{T} = \frac{1000}{1.293} \times \frac{1033}{273} = 2926 \text{ gramme-centimetres.}$$

This is the work done in the expansion of 1 gramme of air at any constant pressure when raised 1° C. in temperature, and its thermal equivalent

$$\frac{2926}{42400} = .0690$$

is the excess of the specific heat at constant pressure above the specific heat at constant volume.

Since the difference of the two thermal capacities of volume V is  $V P/T$ , the *difference of the two thermal capacities of unit volume* is  $P/T$  and *is the same for all gases at the same pressure and temperature*. We neglect here the small departures of actual gases from the simple theoretical laws.

Assuming Regnault's value of the specific heat of air at constant pressure, .2375, the specific heat at constant volume will be

$$.2375 - .0690 = .1685.$$

The heat required to produce a given change or temperature in a gas, when its volume changes in any specified way, may be computed to a very close approximation by calculating the work done by the gas against external resistances during its change of volume, and adding the heat-equivalent of this work to the heat which would have produced the same change of temperature at constant volume.

The above calculation of the difference of the two specific heats rests upon the previously known value of Joule's equivalent. Conversely, from the work done in the expansion of air at constant pressure, combined with the ratio of the two specific heats and the observed value of one of them, the value of Joule's equivalent can be computed. A calculation of this kind, but with an erroneous value of the specific heat of air, was made by Mayer, before Joule's equivalent had been determined.

**211. Thermic Engines.**—In every form of thermic engine, work is obtained by means of expansion produced by heat, the force of expansion being usually applied by admitting a hot elastic fluid to press alternately on opposite sides of a piston travelling in a cylinder. Of the heat received by the elastic fluid from the furnace, a part leaks out by conduction through the sides of the containing vessels, another part is carried out by the fluid when it escapes into the air or into the condenser, the fluid thus escaping being always at a temperature lower than that at which it entered the cylinder, but higher than that of the air or condenser into which it escapes; but a third part has disappeared altogether, and ceased to exist as heat, having been spent in the performance of work. This third part is the exact equivalent of the work performed by the elastic fluid in driving the piston,<sup>1</sup> and may therefore be called the *heat utilized*, or the *heat converted*.

<sup>1</sup> If negative work is done by the fluid in any part of the stroke (that is, if the piston presses back the fluid), the algebraic sum of work is to be taken.

The efficiency of an engine may be measured by the ratio of the heat thus converted to the whole amount of heat which enters the engine; and we shall use the word efficiency in this sense.

**212. Carnot's Investigations.**—The first approach to an exact science of thermo-dynamics was made by Carnot in 1824. By reasoning based on the theory which regards heat as a substance, but which can be modified so as to remain conclusive when heat is regarded as a form of energy, he established the following principles:—

I. *The thermal agency by which mechanical effect may be obtained is the transference of heat from one body to another at a lower temperature.* These two bodies he calls the *source* and the *refrigerator*. Adopting the view generally received at that time regarding the nature of heat, he supposed that all the heat received by an engine was given out by it again as heat; so that, if all lateral escape was prevented, all the heat drawn by the engine from the source was given by the engine to the refrigerator, just as the water which by its descent turns a mill-wheel, runs off in undiminished quantity at a lower level. We now know that, when heat is let down through an engine from a higher to a lower temperature, it is diminished in amount by the equivalent of the work done by the engine against external resistances.

He further shows that the amount of work which can be obtained by letting down a given quantity of heat—or, as we should say with our present knowledge, by partly letting it down and partly consuming it in work, is increased by raising the temperature of the source, or by lowering the temperature of the refrigerator; and establishes the following important principle:—

II. *A perfect thermo-dynamic engine is such that, whatever amount of mechanical effect it can derive from a certain thermal agency; if an equal amount be spent in working it backwards, an equal reverse thermal effect will be produced.* This is often expressed by saying that a completely reversible engine is a perfect engine.

By a *perfect engine* is here meant an engine which possesses the maximum of efficiency compatible with the given temperatures of its source and refrigerator; and Carnot here asserts that all completely reversible engines attain this maximum of efficiency. The proof of this important principle, when adapted to the present state of our knowledge, is as follows:—

Let there be two thermo-dynamic engines, A and B, working

between the same source and refrigerator; and let A be completely reversible.—Let the efficiency of A be  $m$ , so that, of the quantity Q of heat which it draws from the source, it converts  $mQ$  into mechanical effect, and gives  $Q - mQ$  to the refrigerator, when worked forwards. Accordingly, when worked backwards, with the help of work  $mQ$  applied to it from without, it takes  $Q - mQ$  from the refrigerator, and gives Q to the source.

In like manner, let the efficiency of B be  $m'$ , so that, of heat  $Q'$  which it draws from the source, it converts  $m'Q'$  into mechanical effect, and gives  $Q' - m'Q'$  to the refrigerator.

Let this engine be worked forwards, and A backwards. Then, upon the whole, heat to the amount  $Q' - Q$  is drawn from the source, heat  $m'Q' - mQ$  is converted into mechanical effect, and heat  $Q' - Q - (m'Q' - mQ)$  is given to the refrigerator.

If we make  $m'Q' = mQ$ , that is, if we suppose the external effect to be nothing, heat to the amount  $Q' - Q$  or  $(\frac{m}{m'} - 1)Q$  is carried from the source to the refrigerator, if  $m$  be greater than  $m'$ , that is, if the reversed engine be the more efficient of the two. If the other engine be the more efficient, heat to the amount  $(1 - \frac{m}{m'})Q$  is transferred from the refrigerator to the source, or heat pumps itself up from a colder to a warmer body, and *that* by means of a machine which is self-acting, for B does work which is just sufficient to drive A. Such a result we are entitled to assume impossible, therefore B cannot be more efficient than A.

Another proof is obtained by making  $Q' = Q$ . The source then neither gains nor loses heat, and the refrigerator gains  $(m - m')Q$ , which is derived from work performed upon the combined engine from without, if A be more efficient than B. If B were the more efficient of the two, the refrigerator would lose heat to the amount  $(m' - m)Q$ , which would yield its full equivalent of external work, and thus a machine would be kept going and doing external work by means of heat drawn from the coldest body in its neighbourhood, a result which cannot be admitted to be possible.

**213. Examples of Reversibility.**—The following may be mentioned as examples of reversible operations.

When a gas expands at constant temperature, it must be supplied from without with a definite amount of heat; and when it returns, at the same temperature, to its original volume, it gives out the same amount of heat.

When a gas expands adiabatically (that is to say, without interchange of heat with other bodies), it falls in temperature; and when it is compressed adiabatically from the condition thus attained to its original volume, it regains its original temperature.

When water at  $0^{\circ}$  freezes, forming ice at  $0^{\circ}$ , under atmospheric pressure, it expands and does external work in pushing back the atmosphere. It also gives out a definite quantity of heat called the latent heat of liquefaction. This ice can be melted at the same pressure and temperature, and in this reverse process it must be supplied with heat equal to that which it formerly gave out. Also, since the shrinkage will be equal to the former expansion, the pressure of the surrounding atmosphere will do work equal to that formerly done against it.

On the other hand, conduction and radiation of heat are essentially irreversible, since in these operations heat always passes from the warmer to the colder body, and refuses to pass in the opposite direction.

**214. Second Law of Thermo-dynamics.**—It follows, from the principle thus established, that all *reversible engines* with the same temperatures of source and refrigerator have the same efficiency, whether the working substance employed in them be steam, air, or any other material, gaseous, liquid, or solid. Hence we can lay down the following law, which is called the second law of thermo-dynamics: *the efficiency of a completely reversible engine is independent of the nature of the working substance, and depends only on the temperatures at which the engine takes in and gives out heat; and the efficiency of such an engine is the limit of possible efficiency for any engine.*

As appendices to this law it has been further established:

1. That when one of the two temperatures is fixed, the efficiency is simply proportional to the difference between the two, provided this difference is very small. This holds good for all scales of temperature.

2. That the efficiency of a reversible engine is approximately  $\frac{T - T'}{T}$ ,  $T$  denoting the upper and  $T'$  the lower temperature between which the engine works, reckoned from absolute zero (§ 50), on the air-thermometer. This is more easily remembered when stated in the following more symmetrical form. Let  $Q$  denote the quantity of heat taken in at the absolute temperature  $T$ ,  $Q'$  the quantity given out at the absolute temperature  $T'$ , and consequently  $Q - Q'$

the heat converted into mechanical effect, then we shall have approximately

$$\frac{Q}{T} = \frac{Q'}{T'} = \frac{Q - Q'}{T - T'}$$

**215. Proof of Formula for Efficiency.**—This important proposition may be established as follows:—

Let the volume and pressure of a given portion of gas be represented by the rectangular co-ordinates of a movable point, which we will call "the indicating point," horizontal distance representing volume, and vertical distance pressure.

When the temperature is constant, the curve which is the locus of the indicating point is called an *isothermal*, and the relation between the co-ordinates is

$$vp = C,$$

where  $C$  is a constant, depending upon the given temperature, and in fact proportional to the absolute temperature by air-thermometer.

When the changes of volume and pressure are adiabatic (§ 219), a given change of volume will produce a greater change of pressure than when they are isothermal, and the curve traced by the indicating point is called an *adiabatic line*. Whenever the given gas gains or loses heat by interchange with surrounding bodies, the indicating point will be carried from one adiabatic line to another; and by successive additions or subtractions of small quantities of heat we can get any number of adiabatic lines as near together as we please. By drawing a number of adiabatic lines near together, and a number of isothermals near together, we shall cut up our diagram into a number of small quadrilaterals which will be ultimately parallelograms.

Let A B C D (Fig. 126) be one of these parallelograms, and let the gas be put through the series of changes represented by A B, B C, C D, D A, all of which, it will be observed, are reversible.

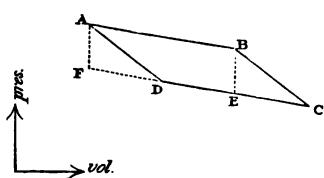


Fig. 126.

In A B the gas expands at constant temperature. Let this temperature, expressed on the absolute scale of the air or gas thermometer, be  $T$ , let the small increase of volume be  $v$ , and the mean pressure  $P$ , so that the work done against external resistances is  $Pv$ .

In BC the gas expands adiabatically and falls in temperature. Let the fall of temperature be  $\tau$ .

In CD it is compressed at the constant temperature  $T - \tau$ .

In DA it is compressed adiabatically, and ends by being in the same state in which it was at the commencement of this cycle of four operations.

Since the external work done by a gas is equal to the algebraic sum of such terms as

$$\text{pressure} \times \text{increase of volume},$$

it is easily shown that the algebraic sum of external work done by the gas in the above cycle is represented by the area of the parallelogram ABCD.

Through A and B draw verticals AF, BE, which, by construction, represent diminution of pressure at constant volume; and produce CD to meet AF in F. Then the area ABCD is equal to the area AB EF (since the parallelograms are on the same base and between the same parallels), that is to AF multiplied by the perpendicular distance between AF and BE. But this perpendicular distance represents  $v$ , the increase of volume from A to B; and AF represents the difference (at constant volume) between the pressure at T and the pressure at  $T + \tau$ . This difference is

$$P \frac{\tau}{T},$$

hence the work done in the cycle is

$$P \frac{\tau}{T} v.$$

But the work done in the operation AB was

$$P v,$$

and this work, being performed at constant temperature, is known (§ 208) to be sensibly equivalent to the whole heat supplied to the gas in the performance of it. This is the only operation in which heat is received from the source, and CD is the only operation in which heat is given out to the refrigerator. Hence we have

$$\frac{\text{heat converted}}{\text{heat from source}} = \frac{P \frac{\tau}{T} v}{P v} = \frac{\tau}{T}.$$

or, if  $Q_1$  represent the heat received from the source,  $Q_2$  the heat given to the refrigerator,  $T_1$  the temperature of the source, and  $T_2$  the temperature of the refrigerator,

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \text{ therefore } \frac{Q_1}{Q_1} = \frac{T_1}{T_1}.$$

This proves the law for any reversible engine with an indefinitely small difference of temperature between source and refrigerator.

Now, let there be a series of reversible engines, such that the first acts as source to the second, the second as source to the third, and so on; and let the notation be as follows:—

The first receives heat  $Q_1$  at temperature  $T_1$ , and gives to the second heat  $Q_2$  at temperature  $T_2$ . The second gives to the third heat  $Q_3$  at temperature  $T_3$ , and so on.

Then supposing the excess of each of these temperatures above the succeeding one to be very small, we have, from above,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad \frac{Q_2}{Q_3} = \frac{T_2}{T_3}, \quad \dots \quad \frac{Q_{n-1}}{Q_n} = \frac{T_{n-1}}{T_n}.$$

Whence, by multiplying equals,

$$\frac{Q_1}{Q_n} = \frac{T_1}{T_n} \text{ therefore } \frac{Q_1 - Q_n}{Q_1} = \frac{T_1 - T_n}{T_1}.$$

The law is therefore proved for the engine formed by thus combining all the separate engines. But this engine is reversible, and therefore (§ 214) the law is true for all reversible engines.

**216. Thomson's Absolute Scale of Temperature.**—In ordinary thermometers, temperatures are measured by the apparent expansion of a liquid in a glass envelope. If two thermometers are constructed, one with mercury and the other with alcohol for its liquid, it is obviously possible to make their indications agree at two fixed temperatures. If, however, the volume of the tube intervening between the two fixed points thus determined be divided into the same number of equal parts in the two instruments, and the divisions be numbered as degrees of temperature, the two instruments will give different indications if plunged in the same bath at an intermediate temperature, and they will also differ at temperatures lying beyond the two fixed points. It is a simple matter to test equality of temperature, but it is far from simple to decide upon a test of equal differences of temperatures. Different liquids expand not only by different amounts but by amounts which are not proportional, no two liquids being in this respect in agreement.

In the case of permanent gases expanding under constant pressure, the discordances are much less, and may, in ordinary circumstances,

be neglected. Hence gases would seem to be indicated by nature as the proper substances by which to measure temperature, if differences of temperature are to be measured by differences of volume.

It is also possible to establish a scale of temperature by assuming that some one substance rises by equal increments of temperature on receiving successive equal additions of heat; in other words, by making some one substance the standard of reference for specific heat, and making its specific heat constant by definition at all temperatures. Here, again, the scale would be different according to the liquid chosen. A mixture of equal weights of water at 0° C. and 100° C. will not have precisely the same temperature as a mixture of equal weights of mercury at these temperatures. If, however, we resort to permanent gases, we find again a very close agreement, so that, if one gas be assumed to have the same specific heat at all temperatures (whether at constant volume or at constant pressure), the specific heat of any other permanent gas will also be sensibly independent of temperature. More than this;—the measurement of temperature by assuming the specific heats of permanent gases to be constant, agrees almost exactly with the measurement of temperature by the expansion of permanent gases. For, as we have seen (§ 69), a permanent gas under constant pressure has its volume increased by equal amounts on receiving successive equal additions of heat.

The air-thermometer, or gas-thermometer, then, has a greatly superior claim to the mercury thermometer to be considered as furnishing a natural standard of temperature.

But a scale which is not only sensibly but absolutely independent of the peculiarities of particular substances, is obtained by *defining temperature in such a sense as to make appendix (2) to the second law of thermo-dynamics rigorously exact*. According to this system, which was first proposed by Thomson (Lord Kelvin), the ratio of any two temperatures is the ratio of the two quantities of heat which would be drawn from the source and supplied to the refrigerator by a completely reversible thermo-dynamic engine working between these temperatures. This ratio will be rigorously the same, whatever the working substance in the engine may be, and whether it be solid, liquid, or gaseous.

217. Temperature estimated in this way is called *absolute thermo-dynamic temperature*, and is almost exclusively employed in thermo-dynamic investigations.

It is not difficult to prove (see a later section on Entropy) that when a reversible engine takes in and gives out heat at any number of different temperatures, the sum of all the quotients  $Q/T$  is zero, for any series of operations which end by leaving the body in the condition in which it was at first;  $Q$  denoting any one of the quantities of heat taken in or given out (reckoned positive if taken in and negative if given out), and  $T$  the temperature at which it is taken in or given out. This result, that the sum of the quotients  $Q/T$  vanishes for any cyclic series of operations, is often quoted as the general statement of the second law of thermo-dynamics, and is the most practically useful statement of the law.

**218. Heat required for Change of Volume and Temperature.**—The amount of heat which must be imparted to a body to enable it to pass from one condition, as regards volume and temperature, to another, is not a definite quantity, but depends upon the course by which the transition is effected. It is, in fact, the sum of two quantities, one of them being *the heat which would be required if the transition were made without external work*—as in Joule's experiment of the expansion of compressed air into a vacuous vessel—and the other being *the heat equivalent to the external work which the body performs in making the transition*. As regards the first of these quantities, its amount, in the case of permanent gases, depends almost entirely upon the difference between the initial and final temperatures, being sensibly independent of the change of volume, as Joule's experiment shows. In the case of liquids and solids, its amount depends, to a very large extent, upon the change of volume, so that, if the expansion which heat tends to produce is forcibly prevented, the quantity of heat required to produce a given rise of temperature is greatly diminished. This contrast is sometimes expressed by saying that expansion by heat involves a large amount of internal work in the case of liquids and solids, and an exceedingly small amount in the case of gases; but the phrase *internal work* has not as yet acquired any very precise meaning.<sup>1</sup>

As an illustration of the different courses by which a transition may be effected, suppose a quantity of gas initially at  $0^{\circ}$  C. and a pressure of one atmosphere, and finally at  $100^{\circ}$  C. and the same pressure, the final volume being therefore 1.366 times the initial volume. Of the innumerable courses by which the transition may be made, we will specify two:—

1st. The gas may be raised, at its initial volume, to such a tem-

perature that, when afterwards allowed to expand against pressure gradually diminishing to one atmosphere, it falls to the temperature 100° C. Or,

2d. It may be first allowed to expand, under pressure diminishing from one atmosphere downwards, until its final volume is attained, and may then, at this constant volume, be heated up to 100°.

In both cases it is to be understood that no heat is allowed to enter or escape during expansion.

Obviously, the first course implies the performance of a greater amount of external work than the second, and it will require the communication to the gas of a greater quantity of heat,—greater by the heat-equivalent of the difference of works.

When a body passes through changes which end by leaving it in precisely the same condition in which it was at first, we are not entitled to assume that the amounts of heat which have entered and quitted it are equal. They are not equal unless the algebraic sum of external work done by the body during the changes amounts to zero. If the body has upon the whole done positive work, it must have taken in more heat than it has given out, otherwise there would be a creation of energy; and if it has upon the whole done negative work, it must have given out more heat than it has taken in, otherwise there would be a destruction of energy. In either case, *the difference between the heat taken in and given out must be the equivalent of the algebraic sum of external work.*

These principles are illustrated in the following sections.

**219. Adiabatic Changes. Heating by Compression, and Cooling by Expansion.**—When a gas is compressed in an absolutely non-conducting vessel, or, more generally, when a gas alters its volume without giving heat to other bodies or taking heat from them, its changes are called *adiabatic* [literally, *without passage across*].

Let unit volume of gas, at pressure  $P$  and absolute temperature  $T$ , receive heat which raises its temperature to  $T + r$  at constant pressure. The increase of volume will be  $\frac{r}{T}$ , and the work done by the gas against external resistance will be  $\frac{Pr}{T}$ .

Next let the gas be compressed to its original volume without entrance or escape of heat, and let the temperature at the end of this second operation be denoted by  $T + \kappa r$ , so that the elevation of temperature produced by the compression is  $(\kappa - 1)r$ . The pressure will now be  $P \frac{T + \kappa r}{T}$ , as appears by comparing the final condition of the gas

with its original condition at the same volume. This may be written  $P(1 + \frac{\kappa\tau}{T})$ , and the mean pressure during the second operation may be taken as half the sum of the initial and final pressures, that is, as  $P(1 + \frac{1}{2}\frac{\kappa\tau}{T})$ . The work done upon the gas by the external compressing forces in the second operation is therefore

$$P(1 + \frac{1}{2}\frac{\kappa\tau}{T})\frac{\tau}{T};$$

or, to the first order of small quantities,  $P_T^\tau$ , which is the same as the work done by the gas in the first operation. Hence, to the first order of small quantities, the heat which has been given to the gas is the same as if the gas had been brought without change of volume from its initial to its final condition. That is to say, the heat which produces an elevation  $\tau$  of temperature, at constant pressure, would produce an elevation  $\kappa\tau$  at constant volume. Hence

$$\frac{\text{Specific heat at constant pressure}}{\text{Specific heat at constant volume}} = \kappa,$$

where  $\kappa$  is defined by the condition that  $\kappa - 1$  is the ratio of the elevation of temperature produced by a small adiabatic compression to the elevation of temperature which would be required to produce an equal expansion at constant pressure.

**220. Relations between Adiabatic Changes of Volume, Temperature, and Pressure.**—For the sake of greater clearness, we will tabulate the values of volume, temperature, and pressure, at the beginning and end of the adiabatic compression above discussed.

	At beginning.	At end.	Change.
Volume,.....	$1 + \frac{\tau}{T}$	1	$-\frac{\tau}{T}$
Temperature, .....	$T + \tau$	$T + \kappa\tau$	$(\kappa - 1)\tau$
Pressure, .....	$P$	$P(1 + \frac{\kappa\tau}{T})$	$P \frac{\kappa\tau}{T}$

Denoting volume, temperature, and pressure by  $V$ ,  $T$ ,  $P$ , and their changes by  $dV$ ,  $dT$ ,  $dP$ , we have, to the first order of small quantities,

$$\frac{dV}{V} = -\frac{\tau}{T}, \quad \frac{dT}{T} = \frac{(\kappa - 1)\tau}{T}, \quad \frac{dP}{P} = \frac{\kappa\tau}{T}.$$

$\frac{dV}{V}$ ,  $\frac{dT}{T}$ ,  $\frac{dP}{P}$  are therefore proportional to  $-1$ ,  $\kappa - 1$ ,  $\kappa$ ;

that is  $\frac{d \log V}{-1} = \frac{d \log T}{\kappa - 1} = \frac{d \log P}{\kappa}$ ;

whence, if  $V_1, T_1, P_1$  are one set of corresponding values, and  $V_2, T_2, P_2$  another set, we have

$$\left(\frac{V_1}{V_2}\right)^{\kappa-1} = \frac{T_2}{T_1}$$

$$\left(\frac{V_1}{V_2}\right)^\kappa = \frac{P_2}{P_1}$$

**221. Numerical Value of  $\kappa$ .**—Since  $\frac{dP}{P}$  divided by  $-\frac{dV}{V}$  is  $\kappa$ ,  $dP$  divided by  $-dV$  (which, by definition, is the coefficient of elasticity of the gas), is equal to  $P\kappa$ . Now the square of the velocity of sound in a gas can be proved to be equal to the coefficient of elasticity divided by the density, and hence from observations on the velocity of sound the value of  $\kappa$  can be determined. It is thus found that

$$\kappa = 1.408$$

for perfectly dry air; and its value is very nearly the same for all other gases which are difficult to liquefy.

**222. Rankine's Prediction of the Specific Heat of Air.**—Let  $S_1$  denote the specific heat of air at constant pressure, and  $S_2$  its specific heat at constant volume. Then (§§ 220, 221) we have

$$\frac{s_1}{s_2} = 1.408.$$

But we have proved (§ 210) by thermo-dynamic considerations, independent of any direct observation of specific heat that

$$s_1 - s_2 = .0690.$$

From these two equations we have

$$\begin{aligned}s_2(1.408 - 1) &= .0690 \\ s_2 &= \frac{.069}{1.408} = .069 \\ s_1 &= .069 + .069 = .238.\end{aligned}$$

In this way the correct values of the two specific heats of air were calculated by Rankine, before any accurate determinations of them had been made by direct experiment.

**223. Cooling of Air by Ascent. Convective Equilibrium.**—When a body of air ascends in the atmosphere it expands, in consequence of being relieved of a portion of its pressure, and the foregoing principles enable us to calculate the corresponding fall produced in its temperature. For we have

$$-\frac{dT}{T} = -\frac{\kappa-1}{\kappa} \frac{dP}{P}.$$

But if  $x$  denote height above a fixed level, and  $H$  "pressure height," or "height of homogeneous atmosphere," we have (see Part I.)

$$-\frac{dP}{P} = \frac{dx}{H};$$

also  $H$  is proportional to  $T$ , so that if  $H_0, T_0$  denote the values of  $H, T$  at the freezing-point, we have  $H = H_0 \frac{T}{T_0}$ . Thus we have

$$-\frac{dT}{T} = \frac{\kappa - 1}{\kappa} \frac{dx}{H_0 \frac{T}{T_0}}, \text{ or } -\frac{dT}{dx} = \frac{\kappa - 1}{\kappa} \frac{T_0}{H_0}.$$

Expressing height in metres, the value of  $H_0$  will be 7990, and  $-\frac{dT}{dx}$  will denote the fall of temperature per metre of ascent. Thus, remembering that  $T_0$  is 273, we have

$$-\frac{dT}{dx} = \frac{408}{1408} \frac{273}{7990} = \frac{1}{101},$$

that is, the temperature falls by  $\frac{1}{101}$  of a degree Centigrade per metre of ascent, or falls  $1^\circ \text{C}$ . in ascending 101 metres. In descending air, elevation of temperature will be produced at the same rate. The calculation has been made on the supposition that the air is perfectly dry. The value of  $\kappa$  for superheated vapour is probably different from its value for dry air, and thus the presence of vapour may modify the above rate even when no liquid water is present. If ascending air contains vapour which is condensed into cloud by the cold of expansion, the latent heat thus evolved will retard the cooling; and if descending air contains cloud which is dissipated by the heat of compression, this dissipation retards the warming.

The ascent of warm air will not occur when the actual decrease of temperature upwards is slower than that due to cooling by ascent; for air will not rise if the process of rising would make it colder and heavier than the air through which it would have to pass. On the other hand, air is in an unstable condition, and tends to form convection currents, when the decrease of temperature upwards is more rapid than that due to cooling by ascent.

**224. Adiabatic Compression of Liquids and Solids.**—The following investigation, originally published by Lord Kelvin in the *Proceedings of the Royal Society of Edinburgh*, is applicable to liquids and solids as well as to gases.

Let unit volume of a substance be subjected to a cycle of four

small changes, two of them being adiabatic and the other two at constant pressure.

Representing volume by horizontal distance, and pressure by vertical distance, let the sides of the parallelogram ABCD (Fig. 127) represent the four operations, the base AD being very small compared with the altitude.

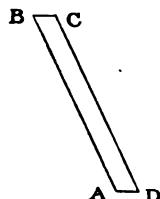


Fig. 127.

Let  $P$  denote the constant pressure in AD, and  $P + p$  the constant pressure in BC, so that  $p$  is represented by the altitude.

AB and CD are adiabatics, and the difference of temperature between B and C will be sensibly equal to that between A and D; call it  $dt$ , and let  $e$  denote the expansion per degree at constant pressure. Then the increase of volume represented by BC or AD is  $e dt$ .

Let the cycle be performed in the direction ABCD. Then the work done by the substance is positive and is represented by the area of the parallelogram, which being the product of base by altitude is  $pe dt$ .

Heat is taken in during the operation BC, as the substance is then expanding at constant pressure, and is given out in DA, each of these quantities of heat being equal to  $C dt$ , where  $C$  denotes the thermal capacity of unit volume of the substance at constant pressure.

Let  $\tau$  denote the excess of temperature of B above A, or of C above D, and  $T$  or  $273 + t$  the absolute temperature. Then the "efficiency" is  $\frac{\tau}{T}$  and is also  $\frac{pe dt}{JC dt}$ , that is  $\frac{pe}{JC}$ , where  $J$  denotes Joule's equivalent. Hence we deduce

$$\frac{\tau}{p} = \frac{Te}{JC};$$

where  $\tau$  is the elevation of temperature produced by the adiabatic increase  $p$  of pressure.

For every substance which expands when heated at constant pressure,  $e$  is positive and therefore  $\tau$  has the same sign as  $p$ , that is, increase of pressure produces elevation of temperature. On the other hand, substances which, like water below  $4^{\circ}$ , contract when heated, are cooled by adiabatic pressure, since  $e$  for such substances is negative.

**225. Adiabatic Extension of a Wire.**—In the above reasoning the

pressure is supposed to be of the nature of hydrostatic pressure, that is, to be equal in all directions. In order to treat the case of stress applied in one direction only, we have merely to modify the meaning of our symbols. The following is the form which the investigation takes when applied to the stretching of a wire.

Let a wire of unit length be subjected to a cycle of four small changes, two of them being adiabatic and the other two at constant tension.

Representing length by horizontal distance, and tension (that is, amount of stretching force,) by vertical distance, let the sides of the parallelogram A B C D (Fig. 128) represent the four operations.

Let  $P$  denote the constant tension in A D, and  $P + p$  the constant tension in B C, so that  $p$  is represented by the altitude.

Let  $dt$  denote the excess of temperature of C above B, or of D above A, and  $e$  the linear expansion per degree at constant tension. Then the increase of length represented by B C or A D is  $e dt$ , the figure being drawn on the supposition that  $e$  is positive. The area of the parallelogram is  $pe dt$ . If the cycle is performed in the direction A B C D, this area represents the work done by the external forces which tend to stretch the wire. As we wish it to represent the work done by the wire against these forces, we shall suppose the cycle to be performed in the opposite direction A D C B. Heat will then be taken in in the operation A D, and given out at a lower temperature in C B.

Let  $T$  be the absolute temperature in the middle of A D, and  $T + \tau$  in the middle of B C, then  $\tau$  will be negative, and by equating the two expressions for the efficiency, we have,

$$-\frac{\tau}{T} = \frac{pe}{JC} \frac{dt}{dt}, \quad \frac{\tau}{p} = -\frac{T\epsilon}{JC}.$$

where C denotes the thermal capacity of the wire at constant tension (the length of the wire being unity), and  $\tau$  is the elevation of temperature produced by the small increase  $p$  of the stretching force.

The signs of  $\tau$  and  $p$  are opposite if  $e$  is positive. Hence every wire that is lengthened by heat will be cooled by the application of tension within its limits of elasticity. If the wire have

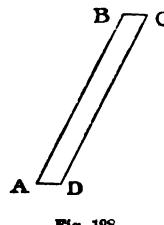


Fig. 128.

unit sectional area, C will denote the capacity of unit volume, and  $p$  the longitudinal stress in units of force per unit of area.

**226. Adiabatic Coefficients of Elasticity.**—Neglecting the exceptional cases of bodies which do not expand with heat, the resistance of a liquid to compression, and the resistance of a solid to both compression and extension, are greater under adiabatic conditions than under the condition of constancy of temperature. Thus, in the circumstances discussed in § 224 the pressure  $p$  produces an elevation of temperature  $\tau$ , and the expansion due to this, namely  $e\tau$ , must be subtracted from the compression which would be produced at constant temperature. This latter is  $\frac{p}{E}$ , where E denotes the coefficient of elasticity at constant temperature; so that the compression will be only  $\frac{p}{E} - e\tau$ . The coefficient of elasticity is in the inverse ratio of the compression; hence, to find the adiabatic coefficient, we must multiply E by

$$\frac{\frac{p}{E}}{\frac{p}{E} - e\tau}, \text{ or by } \frac{1}{1 - \frac{e\tau}{\frac{p}{E}}}.$$

Substituting for  $\tau$  its value  $\frac{Tep}{JC}$ , we find

$$\frac{e\tau}{p} = \frac{e\tau T}{JC}.$$

In assigning the numerical values of E and J, it is to be remembered that if E is expressed in C.G.S. measure, as in the table of elasticities in Part I., the value of J will be 41·6 millions.

The factor for Young's modulus will be of the same form, E now denoting its value at constant temperature, and  $e$  the linear expansion for 1°, while C will still denote the thermal capacity of unit volume, which can be computed by multiplying the specific heat by the density.

**227. Freezing of Water which has been Cooled below 0°.**—We have seen in § 80 that when freezing begins in water which has been cooled below its normal freezing-point, a large quantity of ice is suddenly formed, and the temperature of the whole rises to 0°. In § 81 we have calculated the quantity of ice that will be formed, and we will now revise the calculation in the light of thermodynamics.

The same final condition would have been attained if the whole

mass (unity) of water at  $-t^\circ$  had first been raised in the liquid state to  $0^\circ$ , and the mass  $x$  had then been frozen. The external work would also have been the same, being, in both cases, the product of atmospheric pressure by the excess of the final above the initial volume. Hence the algebraic sum of heat required is the same in both cases. But in the one case it is  $t - 79.25x$ , and in the other case (that is, in the actual case) it is zero. Hence we have

$$t - 79.25x = 0$$

$$x = \frac{t}{79.25}.$$

The calculation in § 81 therefore requires no correction.

**228. Lowering of Freezing-point by Pressure.**—When a litre (or cubic decimetre) of water is frozen under atmospheric pressure, it forms 1.087 of a litre of ice, thus performing external work amounting to  $0.087 \times 103.3 = 9$  kilogramme-decimetres = .9 of a kilogrammetre, since the pressure of one atmosphere or 760 mm. of mercury is 103.3 kilogrammes per square decimetre. Under a pressure of  $n$  atmospheres, the work done would be .9  $n$  kilogrammetres, neglecting the very slight compression due to the increase of pressure. If the ice is allowed to melt in vacuo, no external work is done upon it in the melting, and therefore, in the whole process, at the end of which the water is in the same state as at the beginning, heat to the amount of  $\frac{9n}{424} = 0.00212n$  of a kilogramme-degree is made to disappear. This process is *reversible*, for the water might be frozen in vacuo and melted under pressure; and hence, by appendix (2) to the second law of thermo-dynamics, we have

$$0.00212n : Q :: T - T' : T;$$

where  $Q$  denotes the heat taken in in melting, which is 79.25 kilogramme-degrees,  $T$  the absolute temperature at which the melting occurs, about  $273^\circ$ , and  $T'$  the absolute temperature of freezing under the pressure of  $n$  atmospheres. Hence we have

$$0.00212n : 79.25 :: T - T' : 273;$$

whence

$$T - T' = 0.0073n;$$

that is, the freezing-point is lowered by .0073 of a degree Cent. for each atmosphere of pressure.

**229. Heat of Chemical Combination.**—There is potential energy between the particles of two substances which would combine chemi-

cally if the opportunity were afforded. When *combination* actually takes place, this potential energy runs down and yields an equivalent of heat. We may suppose that the particles rush together in virtue of their mutual attraction, and thus acquire motions which constitute heat.

In every case of *decomposition*, an amount either of heat or some other form of energy must be consumed equivalent to the heat of combination.

When the heat evolved in combination is so great as to produce incandescence, the process is usually called *combustion* or *explosion*, according as it is gradual or sudden. In combustion the action takes place at the surface of contact of the two combining bodies. In explosion they have been previously mingled mechanically, and combination takes place throughout the whole mass.

Chemical combination is often accompanied by diminution of volume, or by change of state from gas or solid to liquid or *vice versa*. These changes sometimes tend to the evolution of heat, as

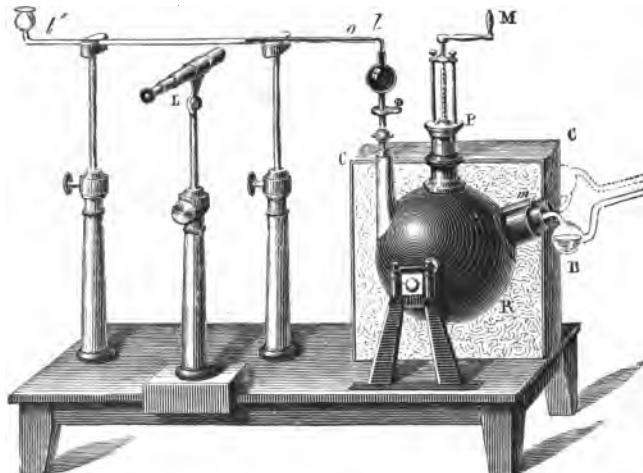


Fig. 129.—Calorimeter of Favre and Silbermann.

when oxygen and hydrogen unite to form liquid water; and sometimes to its absorption, as in freezing-mixtures. The observed thermal effect is therefore the sum or difference of two separate effects; and in general no attempt has been made to assign their respective proportions.

**230. Observations on Heat of Combination.**—Elaborate observa-

tions on the heats of combination of various substances have been made by Andrews, by Favre and Silbermann, and by Thomsen (of Copenhagen). The apparatus chiefly employed by Favre and Silbermann is represented in Fig. 129.

It is a kind of large mercurial thermometer, the reservoir R of which is made of iron, and contains one or more cylindrical openings similar to that shown at *m*. Into these are fitted tubes of glass or platinum, in which the chemical action takes place. One of the substances is introduced first, and the other, which is liquid, is then added by means of a pipette bent at B, and containing the liquid in a globe, as shown in the figure. This is effected by raising the pipette into the position indicated by the dotted lines in the figure.

In the upper part of the reservoir is an opening fitted with a tube containing a steel plunger P, which descends into the mass of mercury, and can be screwed down or up by turning the handle M. To prepare the apparatus for use, the plunger is so adjusted that the mercury stands at the zero-point of the graduated tube *tt'*, the action is then allowed to take place, and the movement of the mercurial column is observed with the telescope L. In order to measure the quantity of heat corresponding to this displacement, a known weight of hot water is introduced into the reservoir, and allowed to give up its heat to the mercury; the displacement of the mercurial column is then observed, and since the quantity of heat corresponding to this displacement is known, that corresponding to any other displacement can easily be calculated. The iron reservoir is inclosed in a box filled with wadding or some other non-conducting material.<sup>1</sup>

When the chemical action takes the form of combustion, a different arrangement is necessary. The apparatus employed by Favre and Silbermann for this purpose is of too complex a construction to be described here. Fig. 130 represents the much simpler apparatus employed for the same purpose by Dulong.

It consists of a combustion-chamber C surrounded by the water contained in a calorimeter D, in which moves an agitator whose stem

<sup>1</sup> In the mode of experimentation adopted by Dr. Andrews, the combination takes place in a thin copper vessel inclosed in a calorimeter of water to which it gives up its heat; and the rise of temperature in the water is observed with a very delicate thermometer, the water being agitated either by stirring with a glass rod or by making the whole apparatus revolve about a horizontal axis.

In experimenting on the heat of combustion, the oxygen and the substance to be burned are introduced into the thin copper vessel, which is inclosed in the calorimeter as above, and ignition or explosion is produced by means of electricity.

is shown at A. The combustible substance, if it be a gas, is conducted into the chamber through the tube *h*, and the oxygen necessary for its combustion enters by one of the tubes *f* or *p'*.

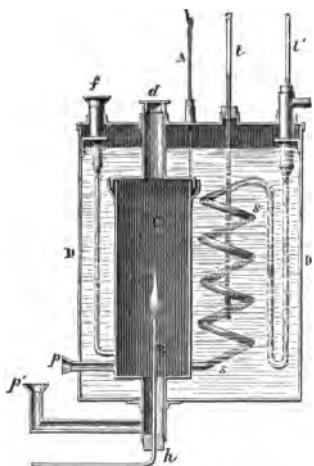


Fig. 130.—Dulong's Calorimeter for Combustion.

The products of combustion pass through the worm *s*, and finally escape, but not until they have fallen to the temperature of the water in the calorimeter. This condition is necessary to the exactness of the result, and its precise fulfilment is verified by observing the temperatures indicated by the thermometers *t* and *t'*, the former of which gives the temperature of the water, and the latter that of the products of combustion at their exit. These two temperatures should always agree. The progress of the combustion is observed through the opening *p*, which is closed by a piece of glass.

The following table exhibits some of the principal results. The numbers denote the mass of water which would be raised  $1^{\circ}$  C. in temperature by the heat evolved in the combustion of unit mass of the substance, the combustion being supposed to take place in air or oxygen, with the exception of the second example on the list.

#### HEATS OF COMBUSTION.

Hydrogen, . . . . .	34,462	Soft sulphur, . . . . .	2,258
Hydrogen with chlorine, .	23,783	Sulphide of carbon, . . .	3,400
Carbonic oxide, . . . . .	3,403	Olefiant gas, . . . . .	11,857
Marsh-gas, . . . . .	13,063	Ether, . . . . .	9,028
Charcoal, . . . . .	8,080	Alcohol, . . . . .	7,184
Graphite, . . . . .	7,797	Stearic acid, . . . . .	9,616
Diamond, . . . . .	7,770	Oil of turpentine, . . . . .	10,852
Native sulphur, . . . . .	2,261	Olive-oil, . . . . .	9,862

Of all substances hydrogen possesses by far the greatest heat of combustion. This fact accounts for the intense heating effects which can be obtained with the oxy-hydrogen blow-pipe, in which an annular jet of hydrogen is completely burned by means of a central jet of oxygen.

**231. Animal Heat and Work.**—We have every reason to believe that animal heat and motions are derived from the energy of chemical combinations, which take place chiefly in the act of respiration, the

most important being the combination of the oxygen of the air with carbon which is furnished to the blood by the animal's food. The first enunciation of this view has been ascribed to Lavoisier. Rumford certainly entertained very clear and correct ideas on the subject, for he says, in describing his experiments on the boring of cannon:—

"Heat may thus be produced merely by the strength of a horse, and, in a case of a necessity, this heat might be used in cooking victuals. But no circumstances could be imagined in which this method of procuring heat would be advantageous; for more heat might be obtained by using the fodder necessary for the support of a horse as fuel."

When the animal is at rest, the heat generated by chemical combination is equal to that given off from its body; but when it works, an amount of heat disappears equivalent to the mechanical effect produced. This may at first sight appear strange, in view of the fact that a man becomes warmer when he works. The reconciliation of the apparent contradiction is to be found in the circumstance that, in doing work, respiration is quickened, and a greater quantity of carbon consumed.

Elaborate experiments on this subject were conducted by Hirn. He inclosed a man in a box containing a tread-mill, the shaft of which passed through the side of the box; and the arrangements were such that the man could either drive the mill against external resistance, by continually stepping from one tread to the next above in the usual way, or could resist the motion of the mill when driven from without, by continually descending the treads, thus doing negative work. Two flexible tubes were connected, one with his nostrils, and the other with his mouth. He inhaled through the former, and exhaled through the latter, and the air exhaled was collected and analysed. The heat given off from his body to the box was also measured with some degree of approximation. The carbon exhaled, and heat generated, were both tolerably constant in amount when the man was at rest. When he was driving the mill by ascending the treads, the heat given out was increased, but the carbon exhaled was increased in a much greater ratio. When he was doing negative work by descending the treads, the heat given out, though less in absolute amount, was greater in proportion to the carbon exhaled, than in either of the other cases.

**232. Vegetable Growth.**—In the growth of plants, the forces of chemical affinity do negative work. Particles which were previously

held together by these forces are separated, and potential energy is thus obtained. When wood is burned, this potential energy is converted into heat.

We are not, however, to suppose that plants, any more than animals, have the power of *creating* energy. The forces which are peculiar to living plants are merely *directive*. They direct the energy of the solar rays to spend itself in separating the carbon and oxygen which exist united in the carbonic acid of the air; the carbon being taken up by the plant, and the oxygen left.

Coal is the remnant of vegetation which once existed on the earth. Thus all the substances which we are in the habit of employing as fuel, are indebted to the sun for the energy which they give out as heat in their combustion.

**233. Solar Heat.**—The amount of heat radiated from the sun is great almost beyond belief. The best measures of it have been obtained by two instruments which are alike in principle—Sir John Herschel's *actinometer* and Pouillet's *pyrheliometer*. We shall describe the latter, which is represented in Fig. 131.



Fig. 131.—Pyrheliometer.

At the upper end, next the sun, is a shallow cylinder composed of very thin copper or silver, filled with water in which the bulb of a thermometer is inserted, the stem being partially inclosed in the hollow tube which supports the cylinder. At the lower end of the tube is a disc equal and parallel to the base of the cylinder. This is intended to receive the shadow of the cylinder, and thus assist the operator in pointing the instrument directly towards the sun. The cylinder is blackened, in order that its absorbing power may be as great as possible.

The instrument, initially at the temperature of the atmosphere, is first placed for five minutes in a position where it is exposed to the sky, but shaded from the sun, and the increase or diminution of its

temperature is observed; suppose it to be a fall of  $\theta^\circ$ . The screen which shaded it from the sun is then withdrawn, and its rise of temperature is observed for five minutes with the sun shining upon it;

call this rise  $T^{\circ}$ . Finally, it is again screened from the sun, and its fall in five minutes is noted;—call this  $\theta^{\circ}$ . From these observations it is inferred, that the instrument, while exposed to the sun, lost  $\frac{\theta+\theta'}{2}$  to the air and surrounding objects, and that the whole heat which it received from the sun was  $T + \frac{\theta+\theta'}{2}$ , or rather was the product of this difference of temperature by the thermal capacity of the cylinder and its contents. This is the heat which actually reaches the instrument from the sun, but a large additional amount has been intercepted by absorption in the atmosphere. The amount of this absorption can be roughly determined by comparing observations taken when the sun has different altitudes, and when the distance traversed in the air is accordingly different. Including the amount thus absorbed, Pouillet computes that *the heat sent yearly by the sun to the earth would be sufficient to melt a layer of ice 30 metres thick, spread over the surface of the earth*; and Sir John Herschel's estimate is not very different.

The earth occupies only a very small extent in space as viewed from the sun; and if we take into account the radiation in all directions, the whole amount of heat emitted by the sun will be found to be about 2100 million times that received by the earth, or sufficient to melt a thickness of two-fifths of a mile of ice per hour over the whole surface of the sun.

**234. Sources of Solar Heat.**—The only causes that appear at all adequate to produce such an enormous effect, are the energy of the celestial motions, and the potential energy of solar gravitation. The motion of the earth in its orbit is at the rate of about 96,500 feet per second. The kinetic energy of a pound of matter moving with this velocity is equivalent to about 104,000 pound-degrees Centigrade, whereas a pound of carbon produces by its combustion only 8080. The inferior planets travel with greater velocity, the square of the velocity being inversely as the distance from the sun's centre; and the energy of motion is proportional to the square of velocity. It follows that a pound of matter revolving in an orbit just outside the sun would have kinetic energy about 220 times greater than if it travelled with the earth. If this motion were arrested by the body plunging into the sun, the heat generated would be about 2800 times greater than that given out by the combustion of a pound of charcoal. We know that small bodies are travelling about in the celestial spaces; for they often become visible to us as meteors, their incan-

descence being due to the heat generated by their friction against the earth's atmosphere; and there is reason to believe that bodies of this kind compose the immense circumsolar nebula called the zodiacal light, and also, possibly, the solar corona which becomes visible in total eclipses. It is probable that these small bodies, being retarded by the resistance of an ethereal medium, which is too rare to interfere sensibly with the motion of such large bodies as the planets, are gradually sucked into the sun, and thus furnish some contribution towards the maintenance of solar heat. But the perturbations of the inferior planets and comets furnish an approximate indication of the quantity of matter circulating within the orbit of Mercury, and this quantity is found to be such that the heat which it could produce would only be equivalent to a few centuries of solar radiation.

Helmholtz has suggested that the smallness of the sun's density—only  $\frac{1}{4}$  of that of the earth—may be due to the expanded condition consequent on the possession of a very high temperature, and that this high temperature may be kept up by a gradual contraction. Contraction involves approach towards the sun's centre, and therefore the performance of work by solar gravitation. By assuming that the work thus done yields an equivalent of heat, he brings out the result that, if the sun were of uniform density throughout, the heat developed by a contraction amounting to only one ten-thousandth of the solar diameter, would be as much as is emitted by the sun in 2100 years.

**235. Sources of Energy available to Man.**—Man cannot produce energy; he can only apply to his purposes the stores of energy which he finds ready to his hand. With some unimportant exceptions, these can all be traced to three sources:—

I. The solar rays.

II. The energy of the earth's rotation.

III. The energy of the relative motions of the moon, earth, and sun, combined with the potential energy of their mutual gravitation.

The fires which drive our steam-engines owe their energy, as we have seen, to the solar rays. The animals which work for us derive their energy from the food which they eat, and thus, indirectly, from the solar rays. Our water-mills are driven by the descent of water, which has fallen as rain from the clouds, to which it was raised in the form of vapour by means of heat derived from the solar rays.

The wind which propels our sailing-vessels, and turns our wind-

mills, is due to the joint action of heat derived from the sun, and the earth's rotation.

The tides, which are sometimes employed for driving mills, are due to sources II. and III. combined.

The work which man obtains, by his own appliances, from the winds and tides, is altogether insignificant when compared with the work done by these agents without his intervention, this work being chiefly spent in friction. It is certain that all the work which they do, involves the loss of so much energy from the original sources; a loss which is astronomically insignificant for such a period as a century, but may produce, and probably has produced, very sensible effects in long ages. In the case of tidal friction, great part of the loss must fall upon the energy of the earth's rotation; but the case is very different with winds. Neglecting the comparatively insignificant effect of aerial tides, due to the gravitation of the moon and sun, wind-friction cannot in the slightest degree affect the rate of the earth's rotation, for it is impossible for any action exerted between parts of a system to alter the angular momentum<sup>1</sup> of the system. The effect of easterly winds in checking the earth's rotation must therefore be exactly balanced by the effect of westerly winds in accelerating it. In applying this principle, it is to be remembered that the couple exerted by the wind is jointly proportional to the force of friction resolved in an easterly or westerly direction, and to the distance from the earth's axis.

**236. Dissipation of Energy.**—From the principles laid down in the present chapter it appears that, although mechanical work can be entirely spent in producing its equivalent of heat, heat cannot be entirely spent in producing mechanical work. Along with the conversion of heat into mechanical effect, there is always the transference of another and usually much larger quantity of heat from a body at a higher to another at a lower temperature. In conduction and radiation heat passes by a more direct process from a warmer to a colder body, usually without yielding any work at all. In these cases, though there is no loss of energy, there is a running to waste as far as regards convertibility; for a body must be hotter than neighbouring bodies, in order that its heat may be available for yielding work. This process of running down to less available forms has been variously styled *diffusion*, *degradation*, and *dissipation* of

<sup>1</sup> The angular momentum is measured by the product of the moment of inertia (see Part I.) and the angular velocity.

energy, and it is not by any means confined to heat. We can assert of energy in general that it often runs down from a higher to a lower grade (that is to a form less available for yielding work), and that, if a quantity of energy is ever raised from a lower to a higher grade, it is only in virtue of the degradation of another quantity, in such sort that there is never a gain, and is generally a loss, of available energy.

This general tendency in nature was first pointed out by Lord Kelvin. It obviously leads to the conclusion that the earth is gradually approaching a condition in which it will no longer be habitable by man as at present constituted.

**237. Kinetic Theory of Gases.**—According to the theory of the constitution of gases which is now generally accepted and is called by the above name, a simple gas consists of a number of very small and exactly equal particles, called atoms or molecules, moving about with various velocities and continually coming into collision with one another and with the sides of the containing vessel. The total volume of the particles themselves is very small compared with the space in which they move, and consequently the time during which a particle is in collision with other particles is a very small part of its whole time.

Each particle is highly elastic. Its shape can be changed by the application of external forces; but it springs back when left to itself and executes vibrations, which we may compare to those of a tuning-fork or a bell. These are the cause of the peculiar features which are detected in the light of an incandescent gas when analysed by the spectroscope. It can also, like any other free body, have a rotatory or spinning motion. The kinetic energy of a particle is accordingly composed of three parts, one due to its vibration, another to its rotation, and a third to its translation. This third part, which is usually greater than the other two, is called the *energy of agitation*. The other two are included together under the name of *internal energy*, which may be defined as the energy of the relative motion of different parts of the same molecule.

In addition to these, we may have movement of the gas as a whole, which is what is meant when in ordinary language we speak of a gas in motion as distinguished from a gas at rest. In this sense, the velocity at any point of a gas is another name for the velocity of the centre of gravity of a small group of molecules surrounding the point. In what follows we leave such velocity out of account.

238. The ratio of the energy of agitation to the internal energy, though it may vary at a given instant from molecule to molecule, or may vary for the same particle from instant to instant, has a definite and permanent value for the aggregate of all the particles — a value independent of changes of pressure or temperature, but not the same for all gases. The symbol  $\beta$  is employed to denote the ratio of the whole kinetic energy of a gas to the energy of agitation, and the value of  $\beta$  for several of the more permanent gases is 1·634.

The heat of a gas is another name for its kinetic energy, that is, for  $\Sigma \frac{1}{2} \beta m v^2$ , or  $\frac{1}{2} \beta m \Sigma v^2$ ,  $v$  denoting the velocity of a molecule,  $m$  its mass, and  $\Sigma$  indicating summation for all the molecules. To reduce the expression for this heat to ordinary thermal units we must divide by Joule's equivalent.

The absolute temperature of a given gas is proportional to the average kinetic energy of its molecules, that is, to the average value of  $\frac{1}{2} \beta m v^2$ , or, omitting constants, to the average value of  $v^2$ . We shall denote the average value of  $v^2$  by  $V^2$ . Its square root  $V$  is called the *velocity of mean square*.

In a mixture of two simple gases the value of  $V^2$  is not the same for them both, but varies inversely as  $m$ ; in other words,  $mV^2$  has the same value for both constituents. Accordingly, in comparing one gas with another  $mV^2$  is taken as the proportional measure of absolute temperature.

239. The equality of the values of  $mV^2$  for the two components of a mixture is not an arbitrary assumption, but a deduction obtained by a very elaborate mathematical investigation from the supposition of two sets of perfectly elastic balls flying about promiscuously amongst each other.

This and other similar calculations which form an important part of the kinetic theory of gases are conducted by what is called the *statistical method*. Large numbers give steadiness to statistics, and the number of molecules in a cubic centimetre of gas is more than a million of millions of millions. As long as a cubic centimetre of gas remains at the same pressure and temperature the statistics of the velocities of its molecules remain permanent. The velocity of each particle changes in the most irregular manner, but the number of its molecules that have velocities lying between given limits (which may be very close together) never changes by more than an infinitesimal part of itself.

Calculation shows that when we attend not merely to the actual velocities but to their components in a given direction, the statistics of such component velocities will be independent of the direction assumed, even when gravity is taken into account.

**240.** The pressure of a gas against the walls of the containing vessel is due to the impacts of its particles against the walls. To compute its amount, let  $u$  denote the component velocity of a molecule normal to one of the sides supposed plane,  $u$  being regarded as positive when the molecule is approaching the side and negative when receding. Let  $u_1$  be a particular positive value of  $u$ , and let the number of molecules in unit volume that have approximately this velocity be  $n_1$ . The number of molecules of velocity  $u_1$  that impinge on unit area of the side in unit time will be the number that occupy a volume  $u_1$ , and will therefore be  $n_1 u_1$ .

Their momentum before striking is their mass  $m n_1 u_1$  multiplied by their velocity  $u_1$ , and is therefore  $m n_1 u_1^2$ . This is reversed by the collision, so that the change of momentum is  $2 m n_1 u_1^2$ . This, being the change of momentum produced in unit time by the reaction of unit area of the wall, is equal to the pressure on unit area due to the impacts of those molecules which we have been considering. But the number of molecules whose normal velocity is  $u_1$  is, by symmetry, the same as the number whose normal velocity is  $-u_1$ , hence  $2 m n_1 u_1^2$  is the sum of such terms as  $mu^2$  for all the molecules for which the value of  $u^2$  is  $u_1^2$ .

Thus the total pressure on unit area is the sum of such terms as  $mu^2$  for all the particles in unit volume; that is, calling the pressure  $p$ ,

$$p = \Sigma mu^2 = m \Sigma u^2. \quad (1)$$

But, from the symmetry of the constitution of a gas,  $\Sigma u^2$  has the same value for all directions of  $u$ . Combining this principle with the principle that the square of a velocity is the sum of the squares of its three rectangular components, we easily deduce  $\Sigma u^2 = \frac{1}{3} \Sigma v^2$ .

Let  $N$  denote the whole number of molecules in unit volume, and  $\rho$  the density of the gas, which is  $Nm$ , then we have:

$$\Sigma u^2 = \frac{1}{3} \Sigma v^2 = \frac{1}{3} N V^2, \quad (2)$$

$$p = m \Sigma u^2 = \frac{1}{3} Nm V^2 = \frac{1}{3} \rho V^2. \quad (3)$$

**241.** This last result enables us to compute the value of  $V$  for any known gas, for it gives

$$V^2 = \frac{3p}{\rho}. \quad (4)$$

Thus in C.G.S. measure we have for hydrogen (see pp. 305, 306),  $p = 1.0136 \times 10^6$ ,  $\rho = 0.00008957$ , whence  $V = 184,300$  cm. per sec. This is about one nautical mile per second.

The value of  $V$  for any gas bears a constant ratio to the velocity of sound in the gas, namely, the ratio  $\sqrt{\frac{p}{\rho}}$ , where  $\kappa$  denotes the ratio of the two specific heats.

Since the energy of agitation in unit volume is  $\frac{1}{2}pV^2$ , and  $p$  is  $\frac{1}{2}\rho V^2$ , these quantities have the same dimensions and are as 3 to 2.

The equation  $p = \frac{1}{2}\rho V^2$  shows that when  $V^2$  (and therefore the absolute temperature) is given,  $p$  varies as  $\rho$ . This is Boyle's law.

Again, it shows that when  $\rho$  is given,  $p$  varies as  $V^2$ , that is, as the absolute temperature; and that, when  $p$  is given,  $\rho$  varies inversely as  $V^2$ ; that is, the volume varies directly as the absolute temperature.

Further, from the equation  $p = \frac{1}{2}NmV^2$  we deduce that when two gases have the same pressure  $p$  and the same temperature (measured by  $mV^2$ ), they have the same number of particles  $N$  in unit volume, and their densities (since  $\rho = Nm$ ) are directly as  $m$  the mass of a single particle of each; that is, the densities (at the same pressure and temperature) are directly as the atomic weights. This is known as Avvogadro's law.

**242.** In questions relating to specific heat it is convenient to make the unit of heat equal to the unit of energy, so that the quantity of heat in a mass  $\Sigma m$  will be not only proportional but equal to  $\frac{1}{2}\beta\Sigma mv^2$ , or to  $\frac{1}{2}\beta V^2\Sigma m$ , and to employ a unit of temperature such that absolute temperature shall be not only proportional but equal to  $mV^2$ . Then, denoting absolute temperature by  $\theta$ , and quantity of heat or energy in unit volume by  $E$ , we have

$$V^2 = \frac{\theta}{m} \quad (5)$$

$$E = \frac{1}{2}\beta V^2 \Sigma m = \frac{1}{2}\beta V^2 \rho = \frac{1}{2}\beta \frac{\rho}{m} \theta = \frac{1}{2}\beta N \theta. \quad (6)$$

$N$  denoting, as before, the number of molecules in unit volume.

The thermal capacity at constant volume, for unit volume of the gas, is defined as  $\frac{dE}{d\theta}$ , and is  $\frac{1}{2}\beta N$ , it being assumed that  $\beta$  is constant. Since  $N$  is the same for all gases at the same temperature and pressure, the thermal capacity per unit volume is the same for all gases that have the same value of  $\beta$ .

The specific heat at constant volume is the thermal capacity of the volume  $\frac{1}{\rho}$ , and is therefore  $\frac{1}{2}\beta N \frac{1}{\rho}$  or  $\frac{1}{2}\frac{\beta}{m}$ . Hence the specific heat

is inversely as the atomic weight, as asserted by the law of Dulong and Petit.

Again we have

$$p = \frac{1}{3} \rho V^2 = \frac{1}{3} \rho_m = \frac{1}{3} N \theta, \quad (7)$$

$$\frac{p}{\theta} = \frac{1}{3m} = \frac{p \times \text{volume of unit mass}}{\theta}. \quad (8)$$

The work done by the gas (initially at unit volume) in expanding against constant pressure  $p$  when  $\theta$  is increased by unity is  $p \times$  increase of volume  $= p \frac{1}{\theta} = \frac{p}{3m}$ . If the original volume be  $\frac{1}{\rho}$  (in which case the mass will be unity) the work in expanding will be  $\frac{1}{3m}$ . Hence, the ratio of the specific heat at constant pressure to that at constant volume is

$$\kappa = \frac{\frac{1}{\rho} + \beta}{\beta} = \frac{2}{3\beta} + 1, \quad (9)$$

giving

$$\beta = \frac{2}{3(\kappa - 1)}. \quad (10)$$

If we assume  $\kappa = 1.408$ , we find  $\beta = 1.634$ .

**243.** The rate at which a gas escapes through a porous partition will be jointly as the number of molecules in unit volume and the mean value of the velocity resolved normal to the partition; or in our notation it will be jointly as  $N$  and the mean value of  $u$ . This latter, though not identical with the square root of the mean value of  $u^2$ , that is, with the square root of  $\frac{1}{3}V^2$ , can be shown to be in a fixed ratio to it. Hence the rate of diffusion will be proportional to  $NV$ . At given temperature and pressure,  $N$  is the same for all gases, hence the rate of diffusion will be directly as  $V$ , that is inversely as  $\sqrt{m}$ , or inversely as the square root of the density  $Nm$ .

**244. Van der Waals' Formula for correcting Boyle's Law.**—In the calculation by which we have obtained the formula  $p = \frac{1}{3} \rho V^2$ , the molecules were treated as indefinitely small. Increased size of the molecules (for given  $V$ ,  $m$ , and  $n$ ) would involve more frequent collision and therefore increased pressure. Calculation shows that the value of  $p$  as corrected for the finite size of the molecules is

$$\frac{\frac{1}{3}\rho V^2}{1-b\rho}, \text{ or } \frac{1}{3}V^2\left(\frac{1}{\rho}-b\right),$$

$b$  being a small quantity which is constant for a given gas.

Again, the theory of capillarity as applied to liquids teaches that the mutual attraction of the molecules which compose the surface-layer of a liquid pulls the surface-layer inwards upon the rest of the liquid, and that the pressure at the outer boundary of the surface-layer is therefore less than the pressure at and within its inner boundary. The same reasoning which leads to this result in the case of liquids is applicable on a diminished scale to gases. Accordingly  $p$  and  $V$  are smallest at the boundary of a gas, and gradually increase for a very small distance inwards. The formula  $p = \frac{1}{3}\rho V^2$  or the corrected formula  $p = \frac{1}{3}V^2\left(\frac{1}{\rho}-b\right)$ , is applicable to the gas as a whole, but will not be true if we employ the value of  $V^2$  for the gas as a whole in combination with the value of  $p$  at the boundary. In practical measurement of  $p$  it is the pressure at the boundary that is measured. This will be less than  $\frac{1}{3}V^2\left(\frac{1}{\rho}-b\right)$  by the pressure due to the skin attraction, which is easily shown to be proportional to  $\rho^2$ , and may be denoted by  $a\rho^2$ ,  $a$  being constant for a given gas. Hence if we make  $p$  stand for the pressure at the bounding surface of the gas, we have

$$\begin{aligned} p + a\rho^2 &= \frac{1}{3}V^2\left(\frac{1}{\rho}-b\right), \text{ or} \\ (p + a\rho^2) \left(\frac{1}{\rho}-b\right) &= \frac{1}{3}V^2. \end{aligned} \quad (11)$$

This investigation is due to Van der Waals, who writes the first member of (11) in the form  $(p + \frac{a}{v^2})(v - b)$ ,  $v$  denoting the volume of unit mass of the gas. According to his theory it is this product, and not the simple product  $pv$ , that is constant at given temperature.

## CHAPTER XVI.

### THERMO-DYNAMICS (CONTINUED).

**245.** To students familiar with the notation and elementary processes of the differential calculus, the deduction of many of the foregoing results can be presented in a more compact form, as follows:—

**246.** We define a *perfect gas* to be one which fulfils the three following conditions:—

First. Boyle's law: that  $vp$  is constant at constant temperature.

Let the temperature  $t$  of the gas be defined as proportional to the product  $vp$  and as increasing by 100 in passing from 0° C. to 100° C. Let  $v$  be taken as the volume of unit mass of the gas at pressure  $p$  and temperature  $t$ . Then our definition of the temperature is expressed by the equation

$$vp = R t, \quad (1)$$

$R$  being independent of  $v$ ,  $p$ , and  $t$ . This gives

$$vd p + p dv = R dt. \quad (2)$$

Second. That the specific heat of the gas (*i.e.* the heat required to raise it through one degree of temperature as thus defined) at constant pressure is the same at all pressures and at all temperatures. We shall denote it by  $s$ .

Third. That the heat which must be given to the gas from without to enable it to expand at constant temperature is the equivalent of the external work done by the gas in its expansion.

We shall employ as our unit of heat the heat equivalent to the unit of work. The heat required for a small increase of volume  $dv$  at constant temperature will then be  $p dv$ . The heat required for a small rise of temperature  $dt$  at constant volume will be  $s' dt$ , if  $s'$  denote the specific heat at constant volume. Superposing these two small changes, we have as the general expression for the heat  $dQ$  required for any small change

$$dQ = s' dt + p dv. \quad (3)$$

We may regard this equation as the expression of our third condition.

247. When the expansion is at constant pressure, (2) gives  $p dv = R dt$ ; and we then have, by (3),

$$dQ = (s' + R) dt.$$

But by the definition of  $s$ ,  $dQ = s dt$ ; hence we have

$$s' + R = s, \quad (4)$$

and as  $R$  and  $s$  are both constant,  $s'$  must be constant; that is to say, the specific heat of our gas at constant volume will be the same at all pressures and at all temperatures. The constant  $R$  may now be replaced by  $s - s'$ .

248. The condition of an adiabatic change is obtained by putting  $dQ = 0$  in (3), and is

$$s' dt + p dv = 0. \quad (5)$$

Substituting for  $p$  its value  $Rt/v$  or  $(s - s')t/v$ , this reduces to

$$s' \frac{dt}{t} + (s - s') \frac{dv}{v} = 0. \quad (6)$$

Eliminating  $t$  and  $dt$  by the help of (1) and (2), this reduces to

$$s' \frac{dp}{p} + s \frac{dv}{v} = 0. \quad (7)$$

Thus  $d \log p$ ,  $d \log t$ , and  $-d \log v$  are proportional to

$$s, s - s', \text{ and } s',$$

as proved in § 220.

249. The external work done by the gas in expanding from volume  $v_1$  to volume  $v_2$  is the integral of  $p dv$  from  $v_1$  to  $v_2$ . But for unit mass of the gas,  $p = Rt/v = (s - s')t/v$ . Hence the expression for the work may be written  $(s - s') \int \frac{t dv}{v}$ .

When the expansion is isothermal, this becomes

$$(s - s') t \int \frac{dv}{v}, \text{ or } (s - s') t \log \frac{v_2}{v_1}. \quad (8)$$

When the expansion is adiabatic,  $p dv$  is  $-s' dt$  by (5). Hence the work in expanding is equal to  $s'$  multiplied by the fall of temperature.

250. In a cycle of four operations AB, BC, CD, DA (Fig. 132), of which AB, CD are isothermal, and BC, DA adiabatic; if  $t_2$  denote the temperature in AB, and  $t_1$  that in CD, the works in BC and DA are  $\pm s'(t_2 - t_1)$ , and destroy one another. The work in AB is

$(s-s')t_2(\log v_b - \log v_A)$ , and that in CD is  $(s-s')t_1(\log v_D - \log v_o)$ . But by (6),

$$\log v_D - \log v_A = \frac{s'}{s-s'} (\log t_2 - \log t_1) = \log v_o - \log v_b. \quad (9)$$

Hence  $\log v_b - \log v_A = \log v_o - \log v_D$ , and the works in AB and CD are as  $t_2$  to  $-t_1$ .

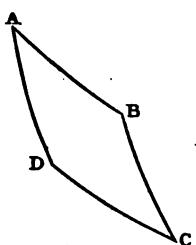


Fig. 132

But by our definition of a perfect gas these amounts of work are equal to the amounts of heat given to the gas from without. Hence the ratio of the heat given to the gas in AB to the heat taken from it in CD is the ratio of the temperature in AB to that in CD when temperature is defined as proportional to  $v_p$  for the gas in question. By the property of reversible engines this ratio is independent of the particular gas employed, and  $t$  as we have defined it is identical with temperature on the absolute thermodynamic scale. Thus all perfect gases must have the same coefficient of expansion.

**251.** We proceed to deal with working substances generally.

From the point of view of thermo-dynamics, two independent variables are just sufficient to specify the condition of a substance. Any two of the three elements—volume, pressure, temperature—will in general determine the third. In the case of a liquid and its vapour present together  $p$  and  $t$  determine each other without reference to  $v$ . Hence  $v$  and  $p$ , or  $v$  and  $t$  will suffice, but  $p$  and  $t$  will not suffice, not being independent; and the same remark applies to a liquid with its solid, or to a solid with its vapour.

**252. Entropy.**—Let AD, BC (Fig. 133) be two adiabatic lines for any substance, and AB, DC two isothermals crossing them. Then since ABCDA represents a Carnot's cycle of reversible operations, the heats taken in or given out by the substance in the two isothermal operations AB, DC are directly as the temperatures at which they are performed. Therefore the heat in AB, divided by the temperature in AB, is equal to the heat in DC, divided by the temperature in DC.

That is to say, if the heat taken in when a substance passes at constant temperature from one adiabatic to another is divided by the temperature, the quotient is the same for all temperatures. This quotient is called the *difference of entropy* of the two

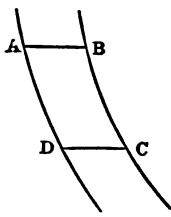


Fig. 133

adiabatics, and if a positive quantity of heat is taken in when the substance passes isothermally from the first of two adiabatics to the second, the second is said to have the greater entropy.

In general when a substance passes by any reversible course from one condition to another, the sum of such terms as  $dQ/t$  is defined to be its gain of entropy,  $dQ$  denoting the small quantity of heat taken in in any element of the course, and  $t$  the temperature at which it is taken in. In travelling along an adiabatic this gain vanishes because  $dQ$  is always zero; hence an adiabatic may also be called an *isentropic* or line of constant entropy. In travelling along an isothermal the definition clearly agrees with our definition of the difference of entropy of two adiabatics.

**253.** In travelling along an irregular course we may by the principle of superposition of small changes replace each small element  $ac$  of the course by two small changes  $ab$ ,  $bc$ , or  $ad$ ,  $dc$  (Fig. 134), one of them isothermal and the other adiabatic. In the adiabatic change the entropy remains constant. In the isothermal change it is increased by the excess of the entropy of the second adiabatic  $cd$  over that of the first  $ab$ . Thus the total gain of entropy in the whole course is the excess of entropy of an adiabatic drawn through the final point above the entropy of an adiabatic drawn through the initial point. It is accordingly independent of the course taken, and entropy, reckoned from an arbitrary condition as zero, is completely determined by the two independent variables which define the body's condition, or may itself be taken as one of the two independent variables. Entropy is usually denoted by the symbol  $\phi$ , so that

$$d\phi = dQ/t, \text{ or } dQ = t d\phi. \quad (10)$$



Fig. 134.

**254.** When heat leaks by conduction or other irreversible process from a body at  $t_2$  to a body at lower temperature  $t_1$ , the colder body gains more entropy than the warmer loses; for if  $dQ$  be the heat which passes,  $dQ/t_1$  is greater than  $dQ/t_2$ . In general, irreversible thermal operations involve gain of entropy in the system as a whole; and the general tendency to "dissipation" of energy may be described as a tendency to increase of entropy. When heat passes by reversible operations from a source to a refrigerator the entropy lost by the source is equal to that gained by the refrigerator.

**255.** The work done in a cycle of two adiabatic and two iso-

thermal operations is equal to the difference of entropy of the two adiabatics multiplied by the difference of temperature of the two isothermals; for, with the notation previously employed, it is  $Q_2 - Q_1 = t_2 Q_2/t_2 - t_1 Q_1/t_1$ , and  $Q_2/t_2$  or its equal  $Q_1/t_1$  is the difference of entropy.

Hence, if we draw a series of adiabatics with a common difference of entropy, and cross them by a series of isothermals with a common difference of temperature, all the meshes of the diagram will be equal in area, for the area of each mesh is equal to the work done in going round it, and this is equal to the common difference of entropy multiplied by the common difference of temperature.

**256.** A number of relations between different thermal properties—relations which must be true for all substances—can be deduced from the well-known mathematical principle that when a function of two independent variables is differentiated first with respect to one of these variables and then with respect to the other, the order of differentiation is indifferent. We shall take four examples.

When a small quantity  $dQ = t d\phi$  of heat is given to a body of unit mass which at the same time expands by the amount  $dv$  at the constant pressure  $p$ , the nett amount of energy given to the body from without (which we will call  $dE$ ) is

$$\begin{aligned} \text{again we have } & dE = t d\phi - p dv \\ \text{and } & d(vp) = v dp + p dv \\ & d(t\phi) = t d\phi + \phi dt \end{aligned} \quad \left. \begin{array}{l} dE = t d\phi - p dv \\ d(vp) = v dp + p dv \\ d(t\phi) = t d\phi + \phi dt \end{array} \right\} \quad (I.)$$

By combining these equations we obtain—

$$d(E + vp) = t d\phi + v dp, \quad (1)$$

$$d(t\phi - E) = p dv + \phi dt, \quad (2)$$

$$d(E + vp - t\phi) = v dp - \phi dt, \quad (3)$$

$$dE = t d\phi - p dv, \quad (4)$$

in which the increments on the left hand, if summed through any course of change, give totals which depend only on the initial and final conditions. This entitles us to apply the principle that the order of differentiation is indifferent. Thus (1), in which  $\phi$  and  $p$  are the two independent variables, gives

$$\frac{dt}{dp}, \text{ for constant } \phi, = \frac{dv}{d\phi}, \text{ for constant } p. \quad (1A)$$

In like manner (2), (3), (4) give

$$\frac{dp}{dt}, \text{ for constant } v, = \frac{d\phi}{dv}, \text{ for constant } t. \quad (2A)$$

$$\frac{dv}{dt}, \text{ for constant } p, = -\frac{d\phi}{dp}, \text{ for constant } t. \quad (3A)$$

$$\frac{dt}{dv}, \text{ for constant } \phi, = -\frac{dp}{d\phi}, \text{ for constant } v. \quad (4A)$$

By substituting  $dQ/t$  for  $d\phi$  these can be reduced to

$$\frac{dt}{t dp} [\text{for constant } \phi] = \frac{dv}{dQ} [\text{for constant } p], \quad (1B)$$

$$\frac{dt}{t dp} [ \quad " \quad v ] = \frac{dv}{dQ} [ \quad " \quad t ], \quad (2B)$$

$$-\frac{dt}{t dv} [ \quad " \quad p ] = \frac{dp}{dQ} [ \quad " \quad t ], \quad (3B)$$

$$-\frac{dt}{t dv} [ \quad " \quad \phi ] = \frac{dp}{dQ} [ \quad " \quad v ]. \quad (4B)$$

In interpreting these results it is not necessary to retain the supposition that the mass acted on is unity, for if the mass were changed the change in  $dv$  would be balanced by the change in  $dQ$ . Constancy of  $\phi$  means adiabatic change, and the student should verify that (1B) is equivalent to the result obtained in § 224 for heating by adiabatic compression. It is to be remembered that  $Q$  is measured in units of work, and that  $t$  is absolute temperature.

257. When the substance is in two states which are present together (liquid and its solid, liquid and its vapour, or solid and its vapour)  $p$  depends on  $t$  only, and conversely  $t$  on  $p$  only, so that constancy of  $p$  is equivalent to constancy of  $t$ . The condition of the substance can still be specified by means of two independent variables, but these must not be  $p$  and  $t$ , though they may be any other two selected from the four  $v, p, t, \phi$ .

Equation (1 B) as applied to this case becomes

$$\frac{dt}{t dp} [\text{unrestricted}] = \frac{dv}{dQ} [\text{constant } p \text{ and } t], \quad (5)$$

and equation (2 B) becomes identical with it.

Equation (3 B) becomes nugatory, both sides vanishing.

Equation (4 B) is not specially modified.

The student should verify that (5) as applied to a mixture of ice and water leads to the result obtained in § 228 for the lowering of the freezing point by pressure. In making the application, using the C.G.S. system,  $dv$  may be taken as  $-087$ ,  $dQ$  as  $80 \times 42 \times 10^6$ ,  $t$  as 273, and for an increase of one atmosphere  $dp$  may be taken as  $10^6$ . These values will be found to give a lowering of 0071 of a degree Cent. per atmosphere.

258. Specific Heat of Saturated Vapour.—Suppose a liquid and its vapour to be present together, the total mass being unity, of which the part  $m$  is vapour, and therefore the part  $1-m$  liquid. We may take  $t$  and  $m$  as the two independent variables. Then a small change of temperature without change of  $m$  would require the addition of heat

$$dQ = \{hm + c(1-m)\} dt,$$

$h$  denoting what is called the *specific heat of the saturated vapour*, and  $c$  the specific heat of the liquid.

A change of  $m$  at constant  $t$  will require the addition

$$dQ = \lambda dm,$$

$\lambda$  denoting the latent heat of evaporation at  $t$ . Hence the general expression for the heat required for a small change is

$$\begin{aligned} dQ &= \{(h-c)m + c\} dt + \lambda dm; && \text{whence} \\ d\phi &= \frac{(h-c)m + c}{t} dt + \frac{\lambda}{t} dm. \end{aligned}$$

The principle that the order of differentiation is indifferent gives, as applied to this expression for  $d\phi$ ,

$$\begin{aligned} \frac{h-c}{t} &= \frac{1}{t} \frac{d\lambda}{dt} - \frac{\lambda}{t^2}, && \text{whence} \\ h &= c + \frac{d\lambda}{dt} - \frac{\lambda}{t}. \end{aligned}$$

This equation is true whatever unit of heat we employ. We may, therefore, employ for steam the value of  $\lambda$  given in (b) § 140, if we put  $t = 273$  for T. This gives approximately

$$\lambda = 800 - 7t.$$

In general if the latent heat of a vapour be expressible as

$$\lambda = a - bt,$$

we have  $\frac{d\lambda}{dt} - \frac{\lambda}{t} = -\frac{a}{t}$ ; whence  $h = c - \frac{a}{t}$ .

For water and steam this gives

$$h = 1 - \frac{800}{t}$$

as the approximate value of the specific heat of saturated steam. It is negative for all values of  $t$  that occur in the practical use of steam.

For saturated vapour by itself we must put  $m=1$ , and if the vapour is to continue just saturated while its volume and temperature change, we must put  $dm=0$ . The general expression for  $dQ$  will then be reduced to

$$dQ = h dt.$$

For every vapour the maximum density increases with the temperature, hence increase of temperature with continuance of saturation implies compression. When  $h$  is negative and  $dt$  positive,  $dQ$  will be negative; hence saturated steam when compressed must be allowed to give out heat if it is to remain just saturated. If compressed adiabatically it will be superheated.

## CHAPTER XVII.

### STEAM AND OTHER HEAT ENGINES.

259. By a heat engine we mean an engine which yields work in virtue of heat supplied to it. The principal heat engines in actual use are the steam-engine and the gas-engine; but air-engines, working by the expansion of air when heated, were at one time in use, and oil-engines in which a spray of oil is converted by heat into vapour are beginning to be employed.

260. Our limits will not permit us to discuss the mechanical details of the various kinds of steam-engine. We must content ourselves with describing the mode in which the pressure of the steam operates to produce mechanical work.

Figs. 135, 136 illustrate the arrangements by which the steam in an ordinary double-acting engine is made to push the piston alternately in opposite directions. Fig. 135 shows the piston P, which works up and down in the cylinder, and is now nearly in the middle of its stroke, being pushed up by steam, which enters through the lower passage  $a'a'$  leading from the steam-chest BB, which is in free communication with the steam-pipe V leading from the boiler. The steam on the upper side of the piston is escaping through the upper passage  $aa$  to the open air or to the condenser. E is the opening leading to the escape-pipe C.

In order to push the piston down again, it is necessary to let steam from the steam-chest enter above the piston, and to let the

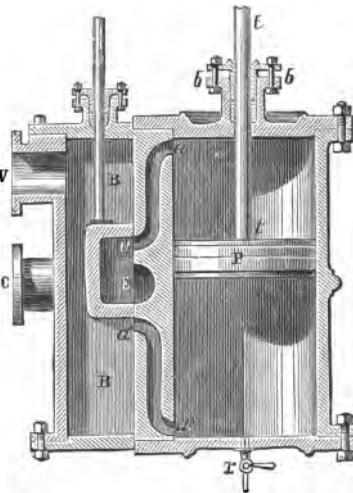


Fig. 135.—Cylinder and Connections.

steam below escape. The way in which this is done is exhibited in Fig. 136, which represents only the parts concerned in directing the course of the steam. There is a movable piece called the *slide-valve*, which slides up and down so as to alter the connections. The first figure shows the position which we have just been considering, the steam being admitted below the piston and allowed to escape

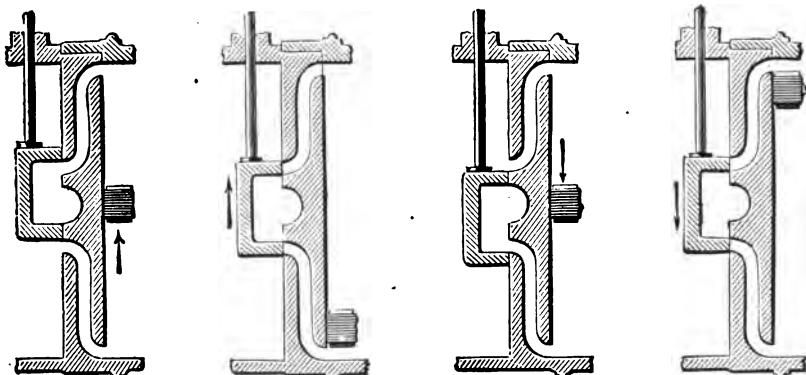


Fig. 136.—Movements of Slide-valve.

above. The second figure shows the slide-valve a little lower down, closing for the instant both passages. The third figure shows the slide-valve still lower; in this position the steam is admitted above the piston and escapes below. In the fourth figure it is again for the instant closing both passages. The slide-valve is in constant motion up and down, being driven by an arrangement (equivalent to a crank) called an *eccentric*, which is shown in duplicate at A, A', Fig. 138, revolving about the point O as centre.

**261. Working Expansively.**—If the steam at its full pressure were discharged into the condenser, a great amount of expansive power would obviously be wasted. This power is utilized by what is called *expansive working*. When the piston has performed a part of its stroke, the steam is shut off (or in technical phrase *cut off*) from the cylinder, and the expansive force of the steam already admitted is left to urge the piston through the remainder of its course. The part of the stroke at which the cut-off occurs may be determined at pleasure. It is sometimes at half-stroke, sometimes at quarter-stroke, sometimes at one-fifth of stroke. In the latter case the piston describes the remaining four-fifths of the stroke under the gradually diminishing pressure of the steam which entered the

cylinder during the first fifth; and the work done during these four-fifths is so much work gained by working expansively.

The cutting off of the steam before the end of the stroke is usually effected by the contrivance represented in Fig. 137: *ad, a'd'*, are two plates forming part of the slide-valve and of much greater width than the openings *L, L'*. The excess of width is called *lap*. By this arrangement one of the apertures is kept closed for some time, so that the steam is shut off, and acts only by expansion. The expansion increases with the lap, but not in simple proportion, as equal movements of the slide-valve do not correspond to equal movements of the piston. The amount of expansion can also be regulated by the *link-motion*, which will be described in § 265.

**262. Compound Engines.**—This is the name given to engines in which the steam, instead of escaping from the cylinder into the condenser, or into the open air, escapes into a second cylinder of larger section than the first, in which it drives a second piston.

In triple-expansion engines, which are now in general use for ocean-going steamers, the steam, when it has driven the piston in the second cylinder, escapes into a third cylinder of still larger section, in which it drives a third piston before passing into the condenser. In the boiler and first cylinder the steam is at very high pressure and temperature (the boiler pressure being usually above 10 atmospheres). As it is worked expansively, it escapes into the second cylinder at a more moderate pressure and temperature, and into the third at a still lower pressure and temperature. If the same amount of total expansion occurred in a single cylinder, it would cool the cylinder too far below the temperature of the entering steam, which would thus be chilled on entering, and thereby deprived of a great portion of its pressure.

Expansive working is often combined with the *superheating* of steam, that is to say, heating the steam on its way from the boiler to the cylinder, so as to raise its temperature above the point of saturation.

**263.** In the construction of the boiler it is important to afford the greatest possible facility for the communication of heat from the furnace to the water. In the locomotive and in many other modern

engines this is effected by making the hot gases on their way from the furnace to the chimney pass through a large number of parallel tubes of copper or other good conductor, which traverse the boiler from end to end and are surrounded by the water. A very large heating surface is thus obtained, and the transmission of heat is proportionally rapid.

**264. Surface Condensation.**—In many modern engines, the condenser consists of a number of vertical tubes of about half an inch diameter, connected at their ends, and kept cool by the external contact of cold water. The steam, on escaping from the cylinder, enters these tubes at their upper ends, and becomes condensed in its passage through them, thus yielding distilled water, which is pumped back to feed the boiler. The same water can thus be put through the engine many times in succession, and the waste which occurs is usually repaired by adding from time to time a little distilled water prepared by a separate apparatus.

The old method of condensing is by a jet of cold water playing into the interior of the condenser.

**265. Apparatus for Reversing: Link-motion.**—The method usually employed for reversing engines is known as Stephenson's link-motion, having been first employed in locomotives constructed by Robert Stephenson, son of the maker of the "Rocket." The merit of the invention belongs to one or both of two workmen in his employ—Williams, a draughtsman, who first designed it, and Howe, a pattern-maker, who, being employed by Williams to construct a model of his invention, introduced some important improvements.

The link-motion, which is represented in Fig. 138, serves two purposes: first, to make the engine travel forwards or backwards at pleasure; and, secondly, to regulate the amount of expansion which shall take place in the cylinder. Two oppositely placed eccentrics, A and A', have their connecting-rods jointed to the two extremities of the *link* B B', which is a curved bar, having a slit, of uniform width, extending along nearly its whole length. In this slit travels a stud or button C, forming part of a lever, which turns about a fixed point E. The end D of the lever D E is jointed to the connecting-rod D N, which moves the rod P of the slide-valve. The link itself is connected with an arrangement of rods L I K H,<sup>1</sup> which enables the

<sup>1</sup> I is a fixed centre of motion, and the rods K I, M I are rigidly connected at right angles to each other. M is a heavy piece, serving to counterpoise the link and eccentric rods.

engine-driver to raise or lower it at pleasure by means of the handle G H F. When the link is lowered to the fullest extent, the end B of the connecting-rod, driven by the eccentric A, is very near the runner C which governs the movement of the slide-valve; this valve accordingly, which can only move in a straight line, obeys the eccentric A almost exclusively. When the link is raised as much as possible, the slide-valve obeys the other eccentric A', and this change

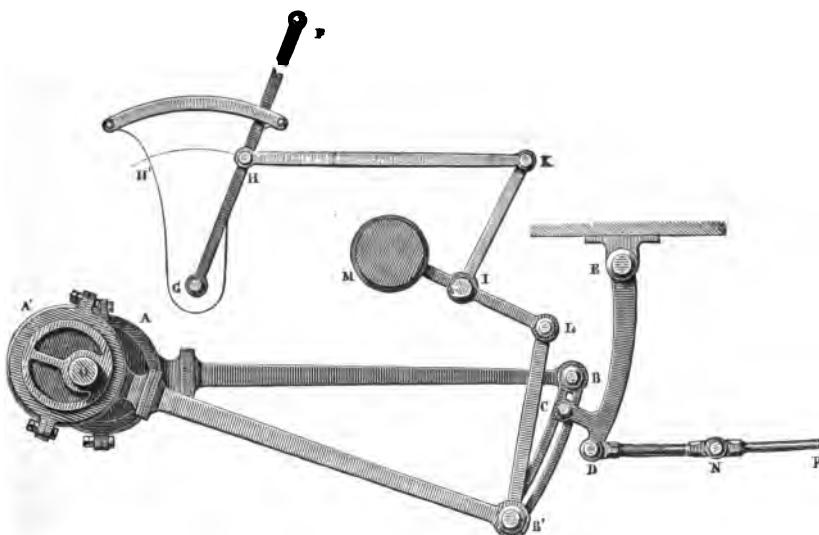


Fig. 138.—Link-motion.

reverses the engine. When the link is exactly midway between the two extreme positions, the slide-valve is influenced by both eccentrics equally, and consequently remains nearly stationary in its middle position, so that no steam is admitted to the cylinder, and the engine stops. By keeping the link near the middle position, steam is admitted during only a small part of the stroke, and consequently undergoes large expansion. By moving it nearer to one of its extreme positions, the travel of the slide-valve is increased, the ports are opened wider and kept open longer, and the engine will accordingly be driven faster, but with less expansion of the steam. As a means of regulating expansion, the link-motion is far from perfect, but its general advantages are such that it has come into very extensive use, not only for locomotives but for all engines which need reversal.

**266. Gas-engines.**—In Otto's "Silent Gas-engine," the earliest type of the class of engine now employed, a dilute mixture of gas and air (about one part in twelve being gas) is admitted into the cylinder, and, after being compressed to about three atmospheres, is ignited by instantaneous communication with a small jet of gas kept constantly burning. The effect is something intermediate between ignition and explosion; the maximum pressure in the early part of the stroke being 10 or 12 atmospheres, and the mean pressure in the whole stroke 4 or 5. In the return stroke, the products of combustion escape at atmospheric pressure, this return stroke being effected by the momentum of the fly-wheel, which also carries the piston through another forward stroke during which the charge of gas and air is admitted, and through another backward stroke in which it is compressed previous to ignition as above described.

This is the ordinary cycle of operations when the engine is working up to the full power for which it is intended; but a centrifugal governor is provided which prevents the gas from being admitted oftener than is necessary for keeping up the standard number of revolutions per minute; so that in working far below its full power the gas is only admitted at every third, fourth, or fifth stroke, the intervening strokes being maintained by the fly-wheel. The governor can be regulated to give any speed required, the most usual being 170 revolutions per minute; and the difference of speed between full work and running idle is only one or two revolutions.

The general appearance of the engine is shown in Fig. 139. A is the cylinder, with a jacket round it through which a convective circulation of water is maintained by means of two pipes, not shown in the figure, connecting it with a tank at a higher level. This is necessary to prevent overheating. C is the centrifugal governor. B, D are two vessels containing oil with automatic lubricators, B lubricates the piston, and D the slide which controls the ignition of the charge. E is a chimney, in the lower part of which the gas jet is kept burning. F is a spring fastening, which keeps the slide strongly pressed home so as to prevent leakage. The connecting-rod, crank, and heavy fly-wheel speak for themselves.

Gas-engines have a great advantage in being constantly ready for use without the tedious process of getting up steam. They are started by lighting the gas jet and giving a few quick turns to the fly-wheel; and are stopped by turning out the jet. The usual sizes are from  $\frac{1}{2}$  to 20 horse-power. They are easily kept in order,

the principal trouble consisting in the removal of a hard deposit of carbon which forms in certain places.

Gas-engines and triple-expansion steam-engines resemble each other in having a very high initial temperature of the expanding

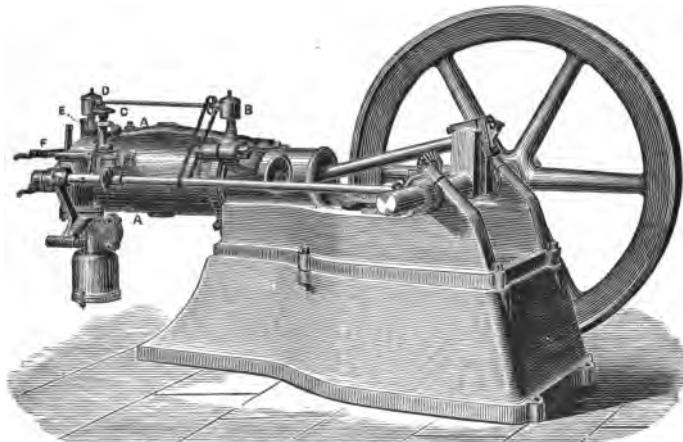


Fig. 139.—Otto's Silent Gas-engine.

fluid which drives the piston, and they resemble each other also in possessing a high degree of "efficiency;" that is to say, they convert a much larger fraction of the heat received into mechanical effect than the simpler forms of steam-engine. But even in the most favourable circumstances this fraction has never, we believe, exceeded one-seventh or thereabouts; so that, from a theoretical point of view, there is still large scope for improvement.

## CHAPTER XVIII.

### TERRESTRIAL TEMPERATURES AND WINDS.

**267. Temperature of the Air.**—By the *temperature of a place* meteorologists commonly understand the *temperature of the air* at a moderate distance (5 or 10 feet) from the ground. This element is easily determined when there is much wind; but in calm weather, and especially when the sun is shining powerfully, it is often difficult to avoid the disturbing effect of radiation. Thermometers for observing the temperature of the air must be sheltered from rain and sunshine, but exposed to a free circulation of air.

**268. Mean Temperature of a Place.**—The *mean temperature of a day* is obtained by making numerous observations at equal intervals of time throughout the day (24 hours), and dividing the sum of the observed temperatures by their number. The accuracy of the determination is increased by increasing the number of observations; as the mean temperature, properly speaking, is the mean of an infinite number of temperatures observed at infinitely short intervals.

If the curve of temperature for the day is given, temperature being represented by height of the curve above a horizontal datum line, the mean temperature is the height of a horizontal line which gives and takes equal areas; or is the height of the middle point of any straight line (terminated by the extreme ordinates of the curve) which gives and takes equal areas.

Attempts have been made to lay down rules for computing the mean temperature of a day from two, three, or four observations at stated hours; but such rules are of very limited application, owing to the different character of the diurnal variation at different places; and at best they cannot pretend to give the temperature of an individual day, but merely results which are correct in the long run. Observations at 9 A.M. and 9 P.M. are very usual in this country; and

the half-sum of the temperatures at these hours is in general a good approximation to the mean temperature of the day. The half-sum of the highest and the lowest temperature in the day, as indicated by maximum and minimum thermometers, is often adopted as the mean temperature. The result thus obtained is usually rather above the true mean temperature, owing to the circumstance that the extreme heat of the day is a more transient phenomenon than the extreme cold of the night. The employment of self-registering thermometers has, however, the great advantage of avoiding errors arising from want of punctuality in the observer. The correction which is to be added or subtracted in order to obtain the true mean from the mean of two observations is called a *correction for diurnal range*. Its amount differs for different places, being usually greatest where the diurnal range itself is greatest.

The *mean temperature of a calendar month* is computed by adding the mean temperatures of the days which compose it, and dividing by their number.

The *mean temperature of a year* is usually computed by adding the mean temperatures of the calendar months, and dividing by 12; but this process is not quite accurate, inasmuch as the calendar months are of unequal length. A more accurate result is obtained by adding the mean temperatures of all the days in the year, and dividing by 365 (or in leap-year by 366).

**269. Isotherms.**—The distribution of temperature over a large region is very clearly represented by drawing upon the map of this region a series of *isothermal lines*; that is, lines characterized by the property that *all places on the same line have the same temperature*. These lines are always understood to refer to mean annual temperature unless the contrary is stated; but isotherms for particular months, especially January and July, are frequently traced, one serving to show the distribution of temperature in winter, and the other in summer. The first extensive series of isotherms was drawn by Humboldt in 1817, on the basis of a large number of observations collected from all parts of the world; and the additional information which has since been collected has not materially altered the forms of the lines traced by him upon the terrestrial globe. They are in many places inclined at a very considerable angle to the parallels of latitude; and nowhere is this deviation from parallelism more observable than in the neighbourhood of Great Britain, Norway, and Iceland—places in this region having the same mean

annual temperature as places in Asia or America lying from 10° to 20° further south.

**270. Insular and Continental Climates.**—We have seen that the specific heat of water, the latent heat of liquid water, and the latent heat of aqueous vapour are all very large. The presence of water accordingly exerts a powerful effect in moderating the extremes both of heat and cold, and a moist climate will in general have a smaller range of temperature than a dry climate. Moreover, since earth and rock are opaque to radiant heat, while water is to a considerable extent diathermanous, the surface of the ground is much more quickly heated and cooled by radiation than the surface of water. This difference is increased by the continual agitation of the surface of the ocean. Large bodies of water thus act as equalizers of temperature, and the most equable climates are found on oceanic islands or on the ocean itself; while the greatest difference between summer and winter is found in the interior of large continents. It is common to distinguish in this sense between *continental* climates on the one hand, and *insular* or *marine* climates on the other.

Some examples of both kinds are given in the following table. The temperatures are Centigrade:—

#### MARINE CLIMATES.

	Winter.	Summer.	Difference.
Faroe Islands, . . . . . .....	8° 90 .....	11° 60 .....	7° 70
Isle of Unst (Shetland), . . ....	4° 05 .....	11° 92 .....	7° 87
Isle of Man, . . . . . .....	5° 59 .....	15° 08 .....	9° 49
Penzance, . . . . . .....	7° 04 .....	15° 83 .....	8° 79
Helston, . . . . . .....	6° 19 .....	16° 00 .....	9° 81

#### CONTINENTAL CLIMATES.

St. Petersburg, . . . . . .....	- 8° 70 .....	15° 96 .....	24° 66
Moscow, . . . . . .....	- 10° 22 .....	17° 55 .....	27° 77
Kasan, . . . . . .....	- 13° 66 .....	17° 35 .....	31° 01
Slatoust, . . . . . .....	- 16° 49 .....	16° 08 .....	32° 57
Irkutsk, . . . . . .....	- 17° 88 .....	16° 00 .....	33° 88
Jakoutsk, . . . . . .....	- 38° 90 .....	17° 20 .....	56° 10

**271. Temperature of the Soil at Different Depths.**—By employing thermometers with their bulbs buried in the earth, and their stems projecting above, numerous observations have been made of the temperature from day to day at different depths from 1 inch to 2 or 3 feet; and at a few places observations of the same kind have been made by means of gigantic spirit-thermometers with exceedingly strong

bulbs, at depths extending to about 25 feet. It is found that variations depending on the hour of the day are scarcely sensible at the depth of 2 or 3 feet, and that those which depend on the time of year decrease gradually as the depth increases, but still remain sensible at the depth of 25 feet, the range of temperature during a year at this depth being usually about 2° or 3° Fahrenheit.

It is also found that, as we descend from the surface, the seasons lag more and more behind those at the surface, the retardation amounting usually to something less than a week for each foot of descent; so that, at the depth of 25 feet in these latitudes, the lowest temperature occurs about June, and the highest about December.

Theory indicates that 1 foot of descent should have about the same effect on diurnal variations as  $\sqrt{365}$  that is 19 feet on annual variations; understanding by *sameness of effect equal absolute amounts of lagging and equal ratios of diminution*.

As the annual range at the surface in Great Britain is usually about 3 times greater than the diurnal range, it follows that the diurnal range at the depth of a foot should be about one-third of the annual range at the depth of 19 feet.

The variations of temperature at the surface are, as every one knows, of a very irregular kind; so that the curve of surface temperature for any particular year is full of sinuosities depending on the accidents of that year. The deeper we go, the more regular does the curve become, and the more nearly does it approach to the character of a simple curve of sines, whose equation can be written

$$y = a \sin. x.$$

Neglecting the departures of the curve from this simple character, theory indicates that, if the soil be uniform, and the surface plane, the annual range (which is equal to  $2a$ ) goes on diminishing in geometrical progression as the depth increases in arithmetical; and observation shows that, if 10 feet be the common difference of depth, the ratio of decrease for range is usually about  $\frac{1}{2}$  or  $\frac{1}{3}$ .

To find a range of a tenth of a degree Fahrenheit, we must go to a depth of from 50 to 80 feet in this climate. At a station where the surface range is double what it is in Great Britain, we should find a range of about two-tenths of a degree at a depth and in a soil which would here give one-tenth.

These remarks show that the phrase "stratum of invariable temperature," which is frequently employed to denote the supposed

lower boundary of the region in which annual range is sensible, has no precise significance, inasmuch as the boundary in question will vary its depth according to the sensitiveness of the thermometer employed.

**272. Increase of Temperature Downwards.**—Observations in all parts of the world show that the temperature at considerable depths, such as are attained in mining and boring, is much above the surface temperature. In sinking a shaft at Rose Bridge Colliery, near Wigan, which is the deepest mine in Great Britain, the temperature of the rock was found to be 94° F. at the depth of 2440 feet. In cutting the Mont Cénis tunnel, the temperature of the deepest part, with 5280 feet of rock overhead, was found to be about 85° F.

The rate of increase downwards is by no means the same everywhere; but it is seldom so rapid as 1° F. in 40 feet, or so slow as 1° F. in 100 feet. The observations at Rose Bridge show a mean rate of increase of about 1° in 55 feet; and this is about the average of the results obtained at other places.

This state of things implies a continual escape of heat from the interior of the earth by conduction, and the amount of this loss per annum can be approximately calculated from the absolute values of conductivity of rock which we have given in Chap. xii.

There can be no reasonable doubt that the decrease of temperature upwards extends to the very surface, when we confine our attention to mean annual temperatures, for all the heat that is conducted up through a stratum at any given depth must also traverse all the strata above it, and heat can only be conducted from a warmer to a colder stratum. Professor Forbes found, at his three stations near Edinburgh, increases of 1°38, 0°96, and 0°19 F. in mean temperature, in descending through about 22 feet, that is, from the depth of 3 to the depth of 24 French feet. The mean annual temperature of the surface of the ground is in Great Britain a little superior to that of the air above it, so far as present observations show. The excess appears to average about 1° F.

**273. Decrease of Temperature Upwards in the Air.**—In comparing the mean temperatures of places in the same neighbourhood at different altitudes, it is found that temperature diminishes as height increases, the rate of decrease for Great Britain, as regards mean annual temperature, being about 1° F. for every 300 feet. A decrease of temperature upwards is also usually experienced in balloon ascents, and numerous observations have been taken for the purpose of deter-

mining its rate. Mr. Glaisher's observations, which are the most numerous as well as the most recent, show that, upon the whole, the decrease becomes less rapid as we ascend higher; also, that it is less rapid with a cloudy than with a clear sky. The following table exhibits a few of Mr. Glaisher's averages:—

Height.	Decrease of Temperature Upwards.	
	With clear sky.	With cloudy sky.
From 0 to 1000 feet, . . .	1° F. in 139 feet.	1° F. in 222 feet.
From 0 to 10,000 ft. . . .	1° F. in 288 feet.	1° F. in 331 feet.
From 0 to 20,000 ft. . . .	1° F. in 365 feet.	1° F. in 468 feet.

These rates may be taken as representing the general law of decrease which prevails in the air over Great Britain in the daytime during the summer half of the year; but the results obtained on different days differ widely, and alternations of increase and decrease are by no means uncommon in passing upwards through successive strata of air. Still more recent observations by Mr. Glaisher, relating chiefly to the first 1000 feet of air, show that the law varies with the hour of the day. The decrease upwards is most rapid soon after midday, and is at this time, and during daytime generally, more rapid as the height is less. About sunset there is a uniform *decrease* at all heights if the sky is clouded, and a uniform *temperature* if the sky is clear. From a few observations which have been taken after sunset, it appears that, with a clear sky, there is an *increase* upwards at night.

That an extremely low temperature exists in the interplanetary spaces, may be inferred from the experimental fact recorded by Sir John Herschel, that a thermometer with its bulb in the focus of a reflector of sufficient size and curvature to screen it from lateral radiation, falls lower when the axis of the reflector is directed upwards to a clear sky than when it is directed either to a cloud or to the snow-clad summits of the Alps. The atmosphere serves as a protection against radiation to these cold spaces, and it is not surprising that, as we increase our elevation, and thus diminish the thickness of the coating of air above us, the protection should be found less complete. But probably the principal cause of the diminution of temperature upwards is the cooling of air by expansion, which we have discussed in § 223.

**274. Causes of Winds.**—The influences which modify the direction and intensity of winds are so various and complicated that anything like a complete account of them can only find a place in treatises specially devoted to that subject. There is, however, one fundamental

principle which suffices to explain the origin of many well-known winds. This principle is plainly illustrated by the following experiment, due to Franklin. A door between two rooms, one heated, and the other cold (in winter), is opened, and two candles are placed, one at the top, and the other at the bottom of the doorway. It is found that the flame of the lower candle is blown towards the heated room, and that of the upper candle away from it.

The principle which this experiment illustrates may be stated as follows:—*When two neighbouring regions are at different temperatures, a current of air flows from the warmer to the colder in the upper strata of the atmosphere; and in the lower strata a current flows from the colder to the warmer.* The reason is that variation of pressure with height is greater in the cold than in the hot region; so that if there be one level at which the pressure is the same in both, the pressure in the cold region will preponderate at lower and that in the hot region at higher levels. We proceed to apply this principle to the land and sea breezes, the monsoons, and the trade-winds.

**275. Land and Sea Breezes.**—At the sea-side during calm weather a wind is generally observed to spring up at about eight or nine in the morning, blowing from the sea, and increasing in force until about two or three in the afternoon. It then begins gradually to die away, and shortly before sunset disappears altogether. A few hours afterwards, a wind springs up in the opposite direction, and lasts till nearly sunrise. These winds, which are called the sea-breeze and land-breeze, are exceedingly regular in their occurrence, though they may sometimes be masked by other winds blowing at the same time. Their origin is very easily explained. During the day the land grows warmer than the water; hence there results a wind blowing towards the warmer region, that is, towards the land. During the night the land and sea both grow colder, but the former more rapidly than the latter; and, accordingly, the relative temperatures of the two elements being now reversed, a breeze blowing from the land towards the sea is the consequence.

**Monsoons.**—The same cause which, on a small scale, produces the diurnal alternation of land and sea breezes, produces, on a larger scale, the annual alternation of monsoons in the Indian Ocean, and the seasonal winds which prevail in some other parts of the world. The general direction of these winds is towards continents in summer, and away from them in winter.

**276. Trade-winds: General Atmospheric Circulation.**—The trade-

winds are winds which blow constantly from a north-easterly quarter over a zone of the northern hemisphere extending from a little north of the tropic of Cancer to within 9 or 10 degrees of the equator; and from a south-easterly quarter over a zone of the southern hemisphere extending from about the tropic of Capricorn to the equator. Their limits vary slightly according to the time of year, changing in the same direction as the sun's declination. Between them is a zone some 5° or 6° wide, over which calms and variable winds prevail.

The cause of the trade-winds was first correctly indicated by Hadley. The greater power of the sun over the equatorial regions causes a continual ascent of heated air from them. This flows over to both sides in the upper regions of the atmosphere, and its place is supplied by colder air flowing in from both sides below. If the earth were at rest, we should thus have a north wind sweeping over the earth's surface on the northern side of the equatorial regions, and a south wind on the southern side. But, in virtue of the earth's rotation, all points on the earth's surface are moving from west to east, with velocities proportional to their distances from the earth's axis. This velocity is nothing at the poles, and increases in approaching the equator. Hence, if a body on the earth's surface, and originally at rest relatively to the earth, be urged by a force acting along a meridian, it will not move along a meridian, but will outrun the earth, or fall behind it, according as its original rotational velocity was greater or less than those of the places to which it comes. That is to say, it will have a relative motion from the west if it be approaching the pole, and from the east if it be approaching the equator.

This would be true, even if the body merely tended to keep its original rotational velocity unchanged, and the reasoning becomes still more forcible when we apply the principle of conservation of angular momentum, in virtue of which the body tends to increase<sup>1</sup> its absolute rotational velocity in approaching the pole, and to diminish it in approaching the equator.

Thus the currents of air which flow in from both sides to the equatorial regions, do not blow from due north and due south, but from north-east and south-east. There can be little doubt that, notwithstanding the variable character of the winds in the temperate and frigid zones, there is, upon the whole, a continual interchange of air between them and the intertropical regions, brought about by the permanent excess of temperature of the latter. Such an interchange,

<sup>1</sup> The tendency is for velocity to vary inversely as distance from the axis of rotation

when considered in conjunction with the difference in the rotational velocities of these regions, implies that the mass of air over an equatorial zone some  $50^{\circ}$  or  $60^{\circ}$  wide, must, upon the whole, have a motion from the east as compared with the earth beneath it; and that the mass of air over all the rest of the earth must, upon the whole, have a relative motion from the west. This theoretical conclusion is corroborated by the distribution of barometric pressure. The barometer stands highest at the two parallels which, according to this theory, form the boundaries between easterly and westerly winds, while at the equator and poles it stands low. This difference may be accounted for by the excess of centrifugal force possessed by west winds, and the defect of centrifugal force in east winds. If the air simply turned with the earth, centrifugal force combined with gravity would not tend to produce accumulation of air over any particular zone, the ellipticity of the earth being precisely adapted to an equitable distribution. But if a body of air or other fluid is moving with sensibly different rotational velocity from the earth, the difference in centrifugal force will give a tendency to move towards the equator, or from it, according as the differential motion is from the west or from the east. The easterly winds over the equatorial zone should therefore tend to remove air from the equator and heap it up at the limiting parallels; and the westerly winds over the remainder of the earth should tend to draw air away from the poles and heap it up at the same limiting parallels. This theoretical consequence exactly agrees with the following table of mean barometric heights in different zones given by Maury:<sup>1</sup>—

North Latitude.	Barometer.	South Latitude.	Barometer.
0° to 5° . . . . .	29.915	0° to 5° . . . . .	29.940
5° to 10° . . . . .	29.922	5° to 10° . . . . .	29.981
10° to 15° . . . . .	29.964	10° to 15° . . . . .	30.028
15° to 20° . . . . .	30.018	15° to 20° . . . . .	30.060
20° to 25° . . . . .	30.081	20° to 25° . . . . .	30.102
25° to 30° . . . . .	30.149	25° to 30° . . . . .	30.095
30° to 35° . . . . .	30.210	30° to 36° . . . . .	30.052
35° to 40° . . . . .	30.124	42° 53' . . . . .	29.90
40° to 45° . . . . .	30.077	45° 0' . . . . .	29.66
45° to 50° . . . . .	30.060	49° 8' . . . . .	29.47
51° 29' . . . . .	29.99	51° 33' . . . . .	29.50
59° 51' . . . . .	29.88	54° 26' . . . . .	29.35
78° 37' . . . . .	29.759	55° 52' . . . . .	29.36
		60° 0' . . . . .	29.11
		66° 0' . . . . .	29.08
		74° 0' . . . . .	28.93

<sup>1</sup> *Physical Geography and Meteorology of the Sea*, p. 180, art. 362, edition 1860.

This table shows that the barometric height falls off regularly on both sides from the two limiting zones  $30^{\circ}$  to  $35^{\circ}$  N. and  $20^{\circ}$  to  $25^{\circ}$  S., the fall continuing towards both poles as far as the observations extend, and continuing inwards to a central minimum between  $0^{\circ}$  and  $5^{\circ}$  N.

If the bottom of a cylindrical vessel of water be covered with saw-dust, and the water made to rotate by stirring, the saw-dust will be drawn away from the edges, and heaped up in the middle, thus showing an indraught of water along the bottom towards the region of low barometer in the centre. It is probable that, from a similar cause (a central depression due to centrifugal force), there is an indraught of air along the earth's surface towards the poles, underneath the primary circulation which our theory supposes; the diminution of velocity by friction against the earth, rendering the lowest portion of the air obedient to this indraught, which the upper strata are enabled to resist by the centrifugal force of their more rapid motion. This, according to Professor James Thomson,<sup>1</sup> is the explanation of the prevalence of south-west winds in the north temperate zone; their southerly component being due to the barometric indraught and their westerly component to differential velocity of rotation. The indraught which also exists from the limiting parallels to the region of low barometer at the equator, coincides with the current due to difference of temperature; and this coincidence may be a main reason of the constancy of the trade-winds.

**277. Origin of Cyclones.**—In the northern hemisphere a wind which would blow towards the north if the earth were at rest, does actually blow towards the north-east; and a wind which would blow towards the south blows towards the south-west. In both cases, the earth's rotation introduces a component towards the right with reference to a person travelling with the wind. In the southern hemisphere it introduces a component towards the left.

Again, a west wind has an excess of centrifugal force which tends to carry it towards the equator, and an east wind has a tendency to move towards the pole; so that here again, in the northern hemi-

<sup>1</sup> The fullest and clearest account, historical and expository, of the theory of general atmospheric circulation is the Bakerian Lecture by Professor James Thomson, *Phil. Trans.*, 1892. Some calculations bearing on the subject will be found in a paper by the editor of the present work in *Phil. Mag.*, Sept. 1871.

sphere the deviation is in both cases to the right, and in the southern hemisphere to the left.

We have thus an explanation of cyclonic movements. In the northern hemisphere, if a sudden diminution of pressure occurs over any large area, the air all around for a considerable distance receives an impetus directed towards this area. But, before the converging streams can meet, they undergo deviation, each to its own right, so that, instead of arriving at their common centre, they blow tangentially to a closed curve surrounding it, and thus produce an eddy from right to left with respect to a person standing in the centre. This is the universal direction of cyclonic rotation in the northern hemisphere; and the opposite rule holds for the southern hemisphere. The former is opposite to, the latter the same as the direction of motion of the hands of a watch lying with its face up. In each case the motion is opposite to the apparent diurnal motion of the sun for the hemisphere in which it occurs.

**278. Anemometers.**—Instruments for measuring either the force or the velocity of the wind are called *anemometers*. Its force is usually measured by Osler's anemometer, in which the pressure of the wind is received upon a square plate attached to one end of a spiral spring (with its axis horizontal), which yields more or less according to the force of the wind, and transmits its motion to a pencil which leaves a trace upon paper moved by clock-work. It seems that the force received by the plate is not rigorously proportional to its size, and that a plate a yard square receives rather more than 9 times the pressure of a plate a foot square. The anemometer which has yielded the most satisfactory results is that invented by the Rev. Dr. Robinson of Armagh, which is represented in Fig. 140, and which indicates the velocity of the wind. It consists of four hemispherical cups attached to the ends of equal horizontal arms, forming a horizontal cross, which turns freely about a vertical axis. By means of an endless screw carried by the axis, a train of wheel-work is set in motion; and the indication is given by a hand which moves round a dial; or, in some instruments, by several hands moving round different dials like those of a gas-meter. The anemometer can also be made to leave a continuous record on paper, for which purpose various contrivances have been successfully employed. It was calculated by the inventor, and confirmed by his own experiments both in air and water, as well as by experiments conducted by Prof. C. Piazzi Smyth at Edinburgh, and more

recently by Sir George Airy at Greenwich, that the centre of each cup moves with a velocity which is almost exactly one-third of that of the wind. This is the only velocity-anemometer whose indications are exactly proportional to the velocity itself. Dr. Whewell's anemometer, which resembles a small windmill, is very far from fulfilling this condition, its variations of velocity being much less than those of the wind.

The direction of the wind, as indicated by a vane, can also be made to leave a continuous record by various contrivances; one of the most common being a pinion carried by the shaft of the vane, and driving a rack which carries a pencil. But perhaps the neatest arrangement for this purpose is a large screw with only one thread

composed of a metal which will write on paper. A sheet of paper is moved by clock-work in a direction perpendicular to the axis of the screw, and is pressed against the thread, touching it of course only in one point, which travels parallel to the axis as the screw turns, and comes back to its original place after one revolution. When one end of the thread leaves the paper, the other end at the same instant comes on. The screw turns with the vane, so that a complete revolution of the screw corresponds to a complete revolution of the wind. This is one of the many ingenious contrivances devised and executed by Mr. Beckley, mechanical assistant in Kew Observatory.

**279. Oceanic Currents.**—The general principle of § 274 applies to liquids as well as to gases; though the effects are usually smaller, owing to their smaller expansibility.

The warm water in the equatorial regions overflows towards the poles, and an under-current of cold water which has descended in the polar regions flows towards the equator. Recent observations

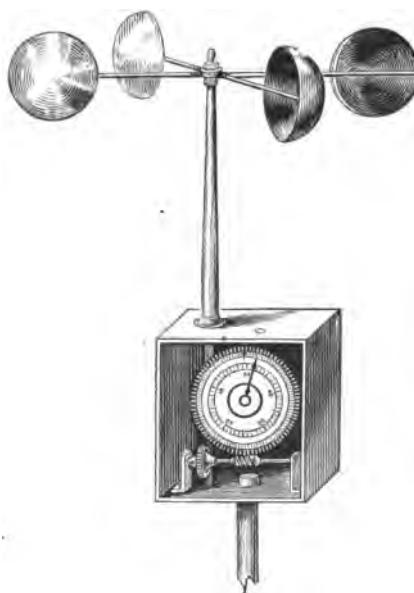


Fig. 140.—Robinson's Anemometer.

have shown that a temperature not much above 0° C. prevails at the bottom of the ocean even between the tropics. A very gradual circulation is thus produced on a very large scale.

The rapid currents which are observed on some parts of the surface of the ocean are probably due to wind. Among these may be mentioned the Gulf Stream. This current of warm water forms a kind of immense river in the midst of the sea, differing in the temperature, saltiness, and colour of its waters from the medium in which it flows. Its origin is in the Gulf of Mexico, whence it issues through the straits between the Bahamas and Florida, turns to the north-west, and splits into two branches, one of which goes to warm the coasts of Ireland and Norway, the other gradually turns southwards, traverses the Atlantic from north to south, and finally loses itself in the regions of the equator.

"The Gulf Stream is a river in the ocean; in the severest droughts it never fails, and in the mightiest floods it never overflows; its banks and its bottom are of cold water, while its current is of warm; it takes its rise in the Gulf of Mexico, and empties into Arctic seas. There is on earth no other such majestic flow of waters. Its current is more rapid than the Mississippi or the Amazon, and its volume more than a thousand times greater. Its waters, as far out from the Gulf as the Carolina coasts, are of indigo blue. They are so distinctly marked that their line of junction with the common sea-water may be traced by the eye. Often one-half of the vessel may be perceived floating in Gulf Stream water, while the other half is in common water of the sea, so sharp is the line."—(Maury, *Physical Geography of the Sea*.)

It would appear that an accumulation of water is produced in the Gulf of Mexico by the trade-wind which blows steadily towards it over the South Atlantic, and that the elevation of level thus occasioned is the principal cause of the Gulf Stream.

# EXAMPLES.

[*The Centigrade Scale is employed, except where otherwise stated.*]

## SCALES OF TEMPERATURE.

1. The difference between the temperatures of two bodies is  $30^{\circ}$  F. Express this difference in degrees Cent. and in degrees Réau.
2. The difference between the temperatures of two bodies is  $12^{\circ}$  C. Express this difference in degrees Réau. and in degrees Fahr.
3. The difference between the temperatures of two bodies is  $25^{\circ}$  R. Express this difference in the Cent. and Fahr. scales.
4. Express the temperature  $70^{\circ}$  F. in the Cent. and Réau. scales.
5. Express the temperature  $60^{\circ}$  C. in the Réau. and Fahr. scales.
6. Express the temperature  $30^{\circ}$  R. in the Cent. and Fahr. scales.
7. Air expands by .00366 of its volume at the freezing-point of water for each degree Cent. By how much does it expand for each degree Fahr.?
8. The temperature of the earth increases by about one degree Fahr. for every 50 feet of descent. How many feet of descent will give an increase of  $1^{\circ}$  Cent., and how many centimetres of descent will give an increase of  $1^{\circ}$  Cent., the foot being  $30\cdot48$  cm.?
9. The mean annual range of temperature at a certain place is  $100^{\circ}$  F. What is this in degrees Cent.?
10. Lead melts at  $326^{\circ}$  C., and in melting absorbs as much heat as would raise  $5\cdot37$  times its mass of water  $1^{\circ}$  C. What numbers will take the place of 326 and  $5\cdot37$  when the Fahrenheit scale is employed?
11. Show that the temperature  $-40^{\circ}$  C. and the temperature  $-40^{\circ}$  F. are identical.
12. What temperature is expressed by the same number in the Fahr. and Réau. scales?

## EXPANSION.

The following coefficients of expansion can be used:—

Linear.	Cubical.
Steel, . . . . .	.0000116
Copper, . . . . .	.0000172
Brass, . . . . .	.0000188
Glass, . . . . .	.0000080
Glass,	.000024
Mercury,	.000179
Alcohol,	.001050
Ether,	.001520

13. The correct length of a steel chain for land measuring is 66 ft. Express, as a decimal of an inch, the difference between the actual lengths of such a chain at  $0^{\circ}$  and  $20^{\circ}$ .

14. One brass yard-measure is correct at  $0^{\circ}$  and another at  $20^{\circ}$ . Find, as a decimal of an inch, the difference of their lengths at the same temperature.
15. A lump of copper has a volume 258 cc. at  $0^{\circ}$ . Find its volume at  $100^{\circ}$ .
16. A glass vessel has a capacity of 1000 cc. at  $0^{\circ}$ . What is its capacity at  $10^{\circ}$ ?
17. A weight-thermometer contains 462 gm. of a certain liquid at  $0^{\circ}$  and only 454 gm. at  $20^{\circ}$ . Find the mean relative expansion per degree between these limits.
18. A weight-thermometer contains 325 gm. of a liquid at zero, and 5 gm. run out when the temperature is raised to  $12^{\circ}$ . Find the mean coefficient of apparent expansion.
19. If the coefficient of relative expansion of mercury in glass be  $\frac{1}{5760}$ , what mass of mercury will overflow from a weight-thermometer which contains 650 gm. of mercury at  $0^{\circ}$  when the temperature is raised to  $100^{\circ}$ ?
20. The capacity of the bulb of a thermometer together with as much of the stem as is below zero is 235 cc. at  $0^{\circ}$ , and the section of the tube is  $\frac{1}{2000}$  sq. cm. Compute the length of a degree (1), if the fluid be mercury; (2), if it be ether.
21. The bulb, together with as much of the stem as is below the zero-point, contains 3·28 gm. of mercury at zero, and the length of a degree is 1 cm. Compute the section of the tube, the density of mercury being about 13·6.
22. What will be the volume at  $300^{\circ}$  of a quantity of gas which occupies 1000 cc. at  $0^{\circ}$ , the pressure being the same?
23. What will be the volume at  $400^{\circ}$  of a quantity of gas which occupies 1000 cc. at  $100^{\circ}$ , the pressure being the same?
24. What will be the pressure at  $30^{\circ}$  of a quantity of gas which at  $0^{\circ}$  has a pressure of a million dynes per sq. cm., the gas being confined in a close vessel whose expansion may be neglected?
25. A thousand cc. of gas at 1·0136 million dynes per sq. cm. are allowed to expand till the pressure becomes a million dynes per sq. cm., and the temperature is at the same time raised from its initial value  $0^{\circ}$  to  $100^{\circ}$ . Find the final volume.
26. A gas initially at volume 4500 cc., temperature  $100^{\circ}$ , and a pressure represented by 75 cm. of mercury, has its pressure increased by 1 cm. of mercury and its temperature raised to  $200^{\circ}$ . Find its final volume.
27. At what temperature will the volume of a gas at a pressure of a million dynes per sq. cm. be 1000 cc., if its volume at temperature  $0^{\circ}$  and pressure 1·02 million dynes per sq. cm. be 1200 cc.?
28. What temperature on the Fahrenheit scale is the absolute zero of the air-thermometer?
29. Find the coefficient of expansion of air per degree Fahrenheit, when  $0^{\circ}$  F. is the starting-point.
30. Express the freezing-point and boiling-point of water as absolute temperatures Fahrenheit.
31. What is the interior volume at  $0^{\circ}$  C. of a glass bulb which at  $25^{\circ}$  C. is exactly filled by 53 grammes of mercury?

FOR DENSITIES OF GASES SEE P. 50.

32. At what temperature does a litre of dry air at 760 mm. weigh 1 grammes?
33. At what temperature will the density of oxygen at the pressure 0·20 m. be the same as that of hydrogen at  $0^{\circ}$  C., at the pressure 1·60 m.?

[The tabulated densities are proportional to the values of  $\frac{DT}{P}$  for the different gases.]

34. What must be the pressure of air at  $15^{\circ}$ , that its density may be the same as that of hydrogen at  $0^{\circ}$  and 760 mm.?

35. A mercurial barometer with brass scale reads at one time 770 mm. with a temperature  $85^{\circ}$ , and at another time 760 mm. with a temperature  $5^{\circ}$ . Find the ratio of the former pressure to the latter.

36. The normal density of air being .000154 of that of brass, what change is produced in the force required to sustain a kilogramme of brass in air, when the pressure and temperature change from 713 mm. and  $-19^{\circ}$  to 781 mm. and  $+36^{\circ}$ ?

37. A cylindrical tube of glass is divided into 300 equal parts. It is loaded with mercury, and sinks to the 50th division from the top in water at  $10^{\circ}$ . To what division will it sink in water at  $50^{\circ}$ , the volumes of a given mass of water at these temperatures being 1.000268 to 1.01205?

38. A closed globe, whose external volume at  $0^{\circ}$  is 10 litres, is immersed in air at  $15^{\circ}$  and at a pressure of 0.77 m. Required (1) the loss of weight which it experiences from the action of the air; (2) the change which this loss would undergo if the pressure became 0.768 m. and the temperature  $17^{\circ}$ .

39. A brass tube contains mercury, with a piece of platinum immersed in it; and the level of the liquid is marked by a scratch on the inside of the tube. On applying heat, it is found that the liquid still stands at this mark. Deduce the ratio of the weight of the platinum to that of the mercury, assuming the density of platinum to be 21.5, and its linear expansion .00001 per degree.

40. A glass tube, closed at one end and drawn out at the other, is filled with dry air, and raised to a temperature  $x$  at atmospheric pressure. It is then hermetically sealed. When it has been cooled to the temperature  $100^{\circ}$  C., it is inverted over mercury, and its pointed end is broken off beneath the surface of the liquid. The mercury rises to the height of 19 centimetres in the tube, the external pressure remaining at 76 cm. as at the commencement of the experiment. The tube is re-inverted, and weighed with the mercury which it contains. The weight of this mercury is found to be 200 grammes; when completely full it contains 300 grammes of mercury. Deduce the temperature  $x$ .

41. A glass tube, whose interior is a right circular cylinder, 2 millimetres in diameter at  $0^{\circ}$  C., contains a column of mercury, whose length at this temperature is 2 decim. What will be the length of this column of mercury when the temperature is  $80^{\circ}$  C.?

42. Some dry air is inclosed in a horizontal thermometric tube, by means of an index of mercury. At  $0^{\circ}$  C. and 0.760 m. the air occupies 720 divisions of the tube, the tube being divided into parts of equal capacity. At an unknown temperature and pressure the same air occupies 960 divisions. The tube being immersed in melting ice, and the latter pressure being still maintained, the air occupies 750 divisions. Required the temperature and pressure.

43. A Graham's compensating pendulum is formed of an iron rod, whose length at  $0^{\circ}$  C. is  $l$ , carrying a cylindrical vessel of glass, which at the same temperature has an internal radius  $r$ , and height  $h$ . Find the depth  $x$  of mercury at  $0^{\circ}$  C. which is necessary for compensation, supposing that the compensation consists in keeping the centre of gravity of the mercury at a constant distance from the axis of suspension.

## THERMAL CAPACITY.

The following values of specific heat can be used :—

Iron, . . . . .	1098	Mercury, . . . . .	·038
Copper, . . . . .	·0949	Alcohol, . . . . .	·548
Platinum, . . . . .	·0385	Ether, . . . . .	·529
Sand, . . . . .	·215	Air, at constant pressure,	·2375
Ice, . . . . .	·504		

44. 17 parts by mass of water at  $5^{\circ}$  are mixed with 23 parts at  $12^{\circ}$ . Find the resulting temperature.

45. 200 gm. of iron at  $300^{\circ}$  are immersed in 1000 gm. of water at  $0^{\circ}$ . Find the resulting temperature.

46. Find the specific heat of a substance 80 gm. of which at  $100^{\circ}$ , when immersed in 200 gm. of water at  $10^{\circ}$  give a resulting temperature of  $20^{\circ}$ .

47. 16 parts by mass of sand at  $75^{\circ}$ , and 20 of iron at  $45^{\circ}$  are thrown into 50 of water at  $4^{\circ}$ . Find the temperature of the mixture.

48. 300 gm. of copper at  $100^{\circ}$  are immersed in 700 gm. of alcohol at  $0^{\circ}$ . Find the resulting temperature.

49. If the length, breadth, and height of a room are respectively 6, 5, and 3 metres, how many gramme-degrees of heat will be required to raise the temperature of the air which fills the room by  $20^{\circ}$ , the pressure of the air being constant, and its average density ·00128 gm. per cubic centimetre?

50. Find the thermal capacities of mercury, alcohol, and ether per unit volume, their densities being respectively 13·6, ·791, and ·716.

## LATENT HEAT.

The following values of latent heat can be used :—

In Melting.	In Evaporation at Atmospheric Pressure.
Water, . . . . .	80
Lead, . . . . .	5·4

51. Find the result of mixing 5 gm. of snow at  $0^{\circ}$  with 23 gm. of water at  $20^{\circ}$ .

52. Find the result of mixing 6 parts (by mass) of snow at  $0^{\circ}$  with 7 of water at  $50^{\circ}$ .

53. Find the result of mixing 3 parts by mass of snow at  $-10^{\circ}$  with 8 of water at  $40^{\circ}$ .

54. Find the result of mixing equal masses of snow at  $-10^{\circ}$  and water at  $60^{\circ}$ .

55. Find the temperature obtained by introducing 10 gm. of steam at  $100^{\circ}$  into 1000 gm. of water at  $0^{\circ}$ .

56. Lead melts at  $320^{\circ}$ . Its specific heat is ·0314 in the solid, and ·0402 in the liquid state. Find what mass of water at  $0^{\circ}$  will be raised one-tenth of a degree by dropping into it 100 gm. of melted lead at  $350^{\circ}$ .

57. What mass of mercury at  $0^{\circ}$  will be raised  $1^{\circ}$  by dropping into it 150 gm. of lead at  $400^{\circ}$ ?

58. A litre of alcohol, measured at  $0^{\circ}$  C., is contained in a brass vessel weighing 100 grammes, and after being raised to  $58^{\circ}$  C., is immersed in a kilogramme

of water at  $10^{\circ}$  C., contained in a brass vessel weighing 200 grammes. The temperature of the water is thereby raised to  $27^{\circ}$ . What is the specific heat of alcohol? The specific gravity of alcohol is 0·8; the specific heat of brass is 0·1.

59. A copper vessel, weighing 1 kilogramme, contains 2 kilogr. of water. A thermometer composed of 100 grammes of glass and 200 gr. of mercury, is completely immersed in this water. All these bodies are at the same temperature,  $0^{\circ}$  C. If 100 grammes of steam at  $100^{\circ}$  C. are passed into the vessel, and condensed in it, what will be the temperature of the whole apparatus when equilibrium has been attained, supposing that there is no loss of heat externally. The specific heat of mercury is 0·033; of copper, 0·095; of glass, 0·177.

#### VARIOUS.

60. A truly conical vessel contains a certain quantity of mercury at  $0^{\circ}$  C. To what temperature must the vessel and its contents be raised that the depth of the liquid may be increased by  $\frac{1}{3}$ , of itself?

61. There is a bent tube, terminating at one end in a large bulb, and simply closed at the other. A column of mercury stands at the same height in the two branches, and thus separates two quantities of air at the same pressure. The air in the bulb is saturated with moisture; that in the opposite branch is perfectly dry. The length of the column of dry air is known, and also its initial pressure, the temperature of the whole being  $0^{\circ}$  C. Calculate the displacement of the mercurial column when the temperature of the apparatus is raised to  $100^{\circ}$  C. The bulb is supposed to have enough water in it to keep the air constantly saturated; and is also supposed to be so large that the volume of the moist air is not sensibly affected by the displacement of the mercurial column.

#### CONDUCTION

(*Units the centimetre, gramme, and second.*)

62. How many gramme-degrees of heat will be conducted in an hour through each sq. cm. of an iron plate 0·2 cm. thick, its two sides being kept at the respective temperatures  $225^{\circ}$  and  $275^{\circ}$ , and the mean conductivity of the iron between these temperatures being 1·2?

63. Through what thickness of copper would the same amount of heat flow as through the 0·2 cm. of iron in the preceding question, with the same temperatures of its two faces, the mean conductivity of the copper between these temperatures being unity?

64. How much heat will be conducted in an hour through each sq. cm. of a plate of ice 2 cm. thick, one side of the ice being at  $0^{\circ}$  and the other at  $-3^{\circ}$ , and its conductivity being 0·0223; and what volume of water at  $0^{\circ}$  would be converted into ice at  $0^{\circ}$  by the loss of this quantity of heat?

65. How much heat will escape in an hour from the walls of a building, if their area be 80 sq. metres, their thickness 20 cm., their material sandstone of conductivity 0·1, and the difference of temperature between outside and inside  $15^{\circ}$ ? What quantity of charcoal burned per hour would generate heat equal to this loss? [see p. 220.]

## HYGROMETRY.

66. A cubic metre of air at  $20^{\circ}$  is found to contain 11.56 grammes of aqueous vapour. What is the relative humidity of this air, the maximum pressure of vapour at  $20^{\circ}$  being 17.39 mm.?

67. Calculate the weight of 15 litres of air saturated with aqueous vapour at  $20^{\circ}$  and 750 mm.

## THERMODYNAMICS.

For the value of Joule's equivalent see § 205.

For heats of combustion see § 230.

68. The labour of a horse is employed for 3 hours in raising the temperature of a million grammes of water by friction. What elevation of temperature will be produced, supposing the horse to work at the rate of  $6 \times 10^9$  ergs per second?

69. From what height (in cm.) must mercury fall at a place where  $g$  is 980, in order to raise its own temperature  $1^{\circ}$  by the destruction of the velocity acquired, supposing no other body to receive any of the heat thus generated?

70. With what velocity (in cm. per sec.) must a leaden bullet strike a target that its temperature may be raised  $100^{\circ}$  by the collision, supposing all the energy of the motion which is destroyed to be spent in heating the bullet?

71. What is the greatest proportion of the heat received by an engine at  $200^{\circ}$  that can be converted into mechanical effect, if the heat which is given out from the engine is given out at the temperature  $10^{\circ}$ ?

72. If a perfect engine gives out heat at  $0^{\circ}$ , at what temperature must it take in heat that half the heat received may be converted?

73. What mass of carbon burned per hour would produce the same quantity of heat as the work of one horse for the same time, a horse-power being taken as  $75 \times 10^8$  ergs per second.

74. A specimen of good coal contains 88 per cent. of carbon and  $4\frac{1}{2}$  per cent. of hydrogen not already combined with oxygen. How many gramme-degrees of heat are generated by the combustion of 1 gm. of this coal; and with what velocity must a gramme of matter move that the energy of its motion may be equal to the energy developed by the combustion of the said gramme of coal?

75. Find the form of the isothermals for steam in contact with water.

76. In the cycle ABCD of § 215 or § 250, show that the volumes and pressures at A and B are proportional to those at D and C.

## ADIABATIC COMPRESSION AND EXTENSION.

77. Find the rise of temperature produced in water at  $10^{\circ}$  C. by an atmosphere of additional pressure, an atmosphere being taken as a million dynes per sq. cm., and the coefficient of expansion at this temperature being .000092.

78. Find the ratio of the adiabatic to the isothermal resistance of water at  $10^{\circ}$  to compression, the value of the latter being  $2.1 \times 10^{10}$  dynes per sq. cm.

79. Find the fall of temperature produced in a wrought iron bar by applying a pull of a million dynes per sq. cm. of section, the coefficient of expansion being .0000122.

80. Find the ratio of the adiabatic to the isothermal resistance of the bar to extension, the value of the latter being  $1.96 \times 10^{12}$  dynes per sq. cm.

## ANSWERS TO EXAMPLES.

**Ex.** 1.  $16\frac{2}{3}$  C.,  $13\frac{1}{3}$  R. **Ex.** 2.  $9\frac{2}{3}$  C.,  $21\frac{2}{3}$  F. **Ex.** 3.  $31\frac{1}{4}$  C.,  $56\frac{1}{4}$  F. **Ex.** 4.  $21\frac{2}{3}$  C.,  $16\frac{2}{3}$  R. **Ex.** 5.  $48^{\circ}$  R.,  $140^{\circ}$  F. **Ex.** 6.  $37\frac{1}{2}$  C.,  $99\frac{1}{2}$  F. **Ex.** 7. .00203. **Ex.** 8. 90 ft., 2743 cm. **Ex.** 9.  $55\frac{2}{3}$  C. **Ex.** 10.  $619^{\circ}$ , 9.666. **Ex.** 12. - $25\cdot 6$ .

**Ex.** 13. 184 in. **Ex.** 14. .0135 in. **Ex.** 15. 259.33 cc. **Ex.** 16. 1000.24 cc. **Ex.** 17. .000881. **Ex.** 18. .001302. **Ex.** 19.  $\frac{650}{88} = 9.85$  gm. **Ex.** 20. (1) .073 cm., (2) .703 cm. **Ex.** 21. .000374 sq. cm.

**Ex.** 22. 2098 cc. **Ex.** 23. 1804 cc. **Ex.** 24. 1.1098 million. **Ex.** 25. 1385 cc. **Ex.** 26. 5631 cc. **Ex.** 27. - $50^{\circ}$ .

**Ex.** 28. - $45^{\circ}$ . **Ex.** 29.  $\frac{1}{4}\pi r^2 h$ . **Ex.** 30.  $491^{\circ}$ ,  $671^{\circ}$ . **Ex.** 31. 3.913 cc. **Ex.** 32.  $80^{\circ}$  C. **Ex.** 33.  $272^{\circ}$ . **Ex.** 34. 55.5 mm. **Ex.** 35.  $759.7 : 759.4$ . **Ex.** 36.  $155 - 140 = .015$  grammes of increase in the apparent weight.

**Ex.** 37.  $47\cdot 3$ . **Ex.** 38. Loss of  $12\cdot 42$  gm., diminished by .12 gm. **Ex.** 39. The ratio of the platinum to the mercury is 4.6 to 1 by volume, and 7.3 to 1 by weight. **Ex.** 40.  $1219^{\circ}$ , neglecting expansions of glass and mercury.

**Ex.** 41. 2.026 decim. **Ex.** 42.  $76\cdot 5$ , 7296 m. **Ex.** 43.  $15l + 1h$ .

**Ex.** 44.  $9\cdot 02$ . **Ex.** 45.  $6\cdot 44$ . **Ex.** 46.  $\frac{5}{16} = 3125$ . **Ex.** 47.  $10^{\circ}$ . **Ex.** 48.  $6\cdot 91$ . **Ex.** 49. 547200. **Ex.** 50. .449, .433, .379.

**Ex.** 51. Water at  $2\frac{1}{2}$ . **Ex.** 52.  $1\frac{1}{2}$  part snow,  $1\frac{1}{2}$  water, all at zero. **Ex.** 53. Water at 5.9. **Ex.** 54. .313 snow,  $1\cdot 687$  water, all at zero. **Ex.** 55. Water at  $6\cdot 3$ . **Ex.** 56. 16600 gm. nearly. **Ex.** 57. 84400 gm. nearly.

**Ex.** 58. .687. **Ex.** 59.  $28\cdot 7$ . **Ex.** 60.  $88^{\circ}$ . **Ex.** 61. The displacement  $x$  is given by the equation  $2x = 753\cdot 7 - \frac{373}{273} \frac{px}{l-x}$ ,  $p$  and  $l$  being the given pressure and length.

**Ex.** 62. 1030000. **Ex.** 63.  $\frac{1}{2}$  cm. =  $1666$  cm. **Ex.** 64. 12.04 gm.-deg., .15 cc. **Ex.** 65. 21600000 gm.-deg., 2673 gm.

**Ex.** 66. 67 per cent. **Ex.** 67.  $17\cdot 68$  gm.

**Ex.** 68.  $1\cdot 56$ . **Ex.** 69. 1401 cm. **Ex.** 70. 16240 cm. per sec. **Ex.** 71.  $\frac{120}{120} = 4$  nearly. **Ex.** 72.  $273^{\circ}$ . **Ex.** 73.  $80\cdot 32$  gm. **Ex.** 74. 8661 gm.-deg., 849000 cm. per sec. nearly.

**Ex.** 75. Straight lines, because pressure is constant.

**Ex.** 76. If  $m$  denote the ratio of the temperature in A B to that in C D, the ratio of the two pressures either at A and D or at B and C is  $m$  raised to the power  $s/(s-s')$ , and the ratio of the volumes is  $1/m$  to the power  $s'/(s-s')$ ; see §§ 220, 250.

**Ex.** 77.  $0\cdot 000626$ . **Ex.** 78.  $1\cdot 0012$ . **Ex.** 79.  $0\cdot 00009$ . **Ex.** 80.  $1\cdot 002$ .



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